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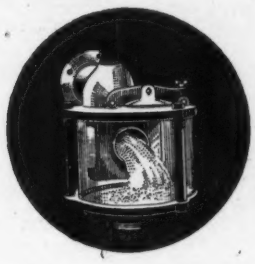


The Look Box

"THE trends in cracking capacities during 1936 were the same as in 1934 and 1935, that is, the capacities operating and under construction increased but the idle capacity declined"—so states a recent release of the Bureau of Mines. Further, the report states "capacity of the operating units, which includes cracking capacity of combination units to which crude is charged, increased from 1,994,868 barrels as of January 1, 1936, to 2,077,325 barrels on January 1, 1937, or 4 percent." The report then points out that "as the charge to cracking stills increased 19 percent in that period, it follows that an increase in the operating ratio outweighed the comparatively small gain in capacity. That the operating ratio for cracking units (80 percent) is approaching the maximum is indicated in the large gain in capacity under construction—30,450 barrels on January 1, 1936, as compared to 138,220 barrels on January 1, 1937. The present amount of new construction in cracking compares with the boom days of 1929 and 1930."

Cracking

It is possible to misinterpret the meaning of this line of discussion. The fact that operating ratio for cracking units, generally accepted as 80 percent of refining capacity, is approaching the maximum, certainly at this time does not presage saturation at an early date with subsequent cessation of cracking-unit construction. Too much old cracking capacity is in operation, too little combination capacity is in existence.

Elsewhere the bureau's report points out that crude-oil capacity of cracking units converted to operate on crude oil and not operating as cracking units, totals 217,885 barrels. No doubt but that considerable cracking capacity will continue to be converted to run on crude oil and much of it after the manner of the new combination units.

At the same time the crude oil capacity of the combination type units has grown to a total of 432,300 barrels. This capacity is still increasing and will continue to increase as the modern combination type system replaces the old cracking units and the old tube stills originally installed to run crude. The total capacity of the more efficient combination type plant is but a small part of total cracking capacity or total crude runs to stills.

Further, a casual study of cracking facilities of the refining companies of this country indicates that around 40 percent of the capacity listed is in bad shape—either of early vintage, it has been subjected to too much corrosive charging stocks, is worn out, or of such type as to be unable to compete in efficiency and flexibility with the modern combination selective cracking system.

Thus there remains a wide spread between modern efficient installations and old-fashioned obsolete installations. Likewise, in any study of processing needs for the refining industry it is well to bear in mind we are still reporting that 25 percent of total crude-oil charging capacity as shell-still operation. Capacity of pipe stills operating on crude was equiv-

alent to about 73 percent of daily average crude runs to stills at the beginning of this year.

Rapid progress has been made in adoption of modern refining methods both for cracking and general distillation, but there remains much yet to be done. Along with constant installation of modern processes for gasoline manufacture, such as the combination selective-cracking type of process, there is likewise a constant depreciation in value of existing older installations due to corrosion and obsolescence.

Business

ALTHOUGH caution and some pessimism have been conspicuous throughout the land during recent weeks, it is difficult to generate much anxiety over the oil industry's outlook.

Late in September it was virtually assured that favorable conditions will prevail at least for several weeks, since close balancing of crude production with market demand is in prospect through October.

While the Bureau of Mines was estimating that 3,568,100 barrels, an increase of 58,000 barrels over its forecast for September, would be needed to meet daily consumption in October, the oil states were getting production matters in hand. Texas, for example, cut back its production allowable 35,890 barrels per day placing its yield at 1,405,844 barrels on the first of the month, which is under the daily recommendation of the bureau.

The Bureau of Mines sees the need for an increase in its estimate of needs for September, which was exceeded by actual production, because of the unusually large export demand. The wars in Europe and the Far East are creating a big consumption of petroleum products, offsetting the seasonal decline caused by less automobile travel.

An important increase in winter motor travel is looked for during the coming months, chiefly because of increased ownership and greater annual use of motor vehicles, the trend toward closed, all-weather cars, and the wide adoption of deferred registration by the states.

By the end of 1937 approximately 30,000,000 motor vehicles, of which about 25,000,000 will be passenger cars, will be registered in this country—a new record high and an increase of about 4,000,000 over 1935. Coupled with this is increasing use of trucks and busses throughout the country and during all seasons. Car owners are tending to use their automobile more each year. The expansion in travel during all seasons can be attributed to closed, all-weather cars, equipped with heaters, windshield defrosters, and other equipment for winter driving which are adding to the comfort of motor travel in cold weather. Snow removal activities of the states and counties are keeping the roads open for travel in the improved cars.

Taxes

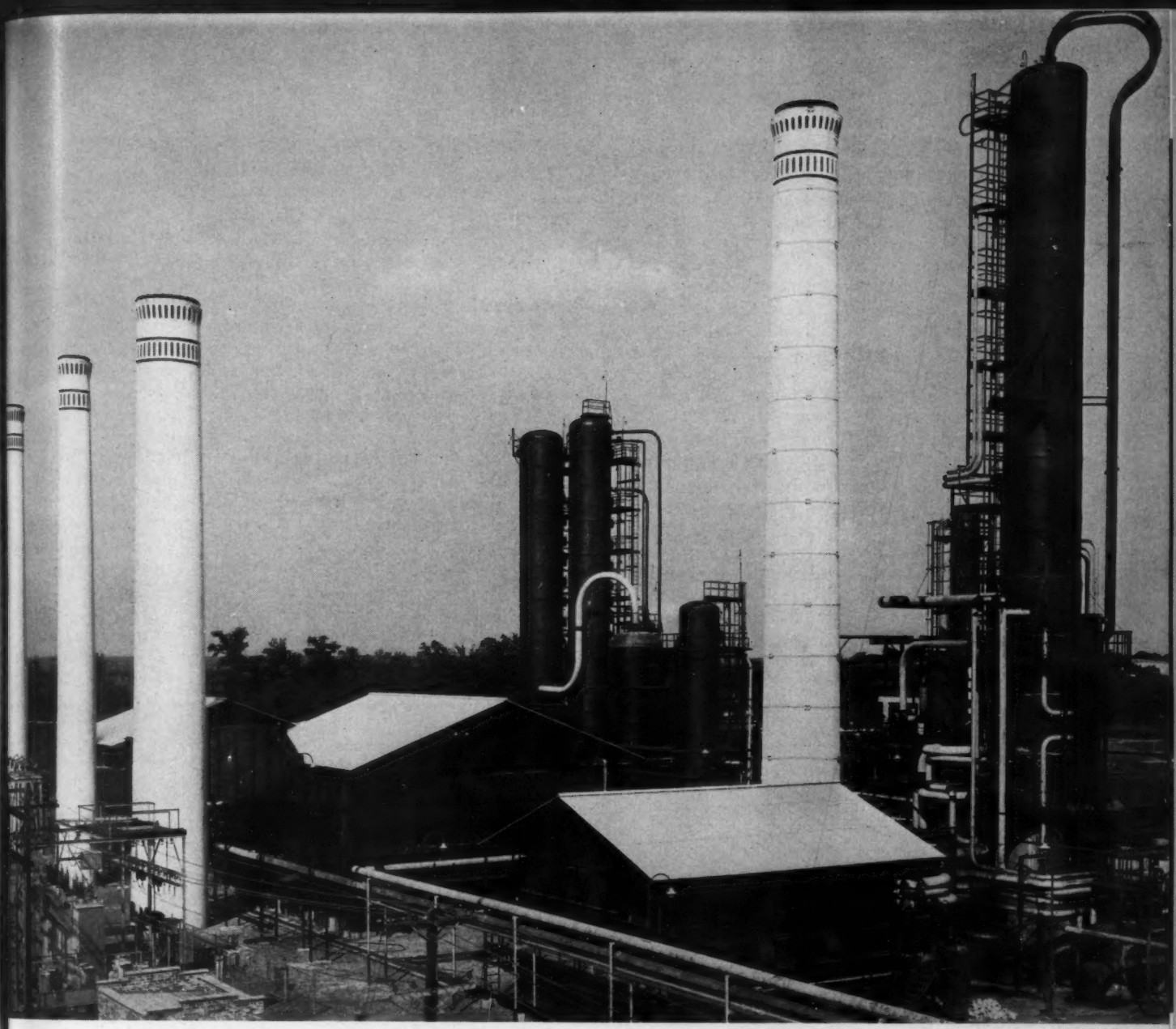
STATE gasoline tax collections are increasing at the rate of $70,000,000 a year because of rapidly expanding automobile ownership and greater annual use of motor vehicles, and as a result of the remarkable gains in road tax revenue many states will be able to reduce their gasoline-tax rates, reports the American Petroleum Industries Committee. Total state gasoline-tax revenues for 1937 will stand at close to $150,000,000 above 1935 collections, the committee estimates. In 1934 state gasoline revenues were $565,027,000, in 1935 they increased by $51,000,000, and in 1936 showed a still further gain of $70,000,000, standing at $691,420,000. Consumption of gasoline in 1937 is showing a gain even larger than last year, and it is expected that the increase in state gasoline revenues will be approximately $75,000,000 for the year.

Because of this remarkable trend of expanding gasoline tax receipts, the committee points out, the states can next year make an average reduction of one cent in their gasoline tax rates without reducing total state gasoline collections below their 1935 level. The industry would like to see such a reduction, so would the motoring public. Perhaps something may come of it.

Building

THE petroleum refining industry, never built, is always building. With the return of better times and with profit-making conditions existing, the industry has extended itself recently with marked increase in construction activities throughout the world.

This work includes replacement of obsolete and worn-out processes, modernization and repair and adoption of the newer processes available. The trend continues toward the more widespread use of high-pressure, high-temperature operating systems, which though costly are necessary for the production of the larger quantities of high-quality motor fuels demanded. Engineering and technical development is so rapid that processes now six to eight years old are considered obsolete. The three conditions—better times, rapid obsolescence, corrosion of equipment make possible and necessary continued expenditures by this branch of the petroleum industry in practically all refining districts in this country and in most of the foreign countries which have refining industries.



Plant Performance *of Modern Combination* Selective Cracking

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Plant data on various crudes are presented demonstrating the results obtained in actual refinery practice by applying the principles of combination selective cracking. These principles are briefly discussed and illustrated by a flow sheet of a modern unit recently put into operation. Plot plan arrangement is also shown along with details of heater design and plant photographs. A discussion of the operating data on three crudes of widely differing characteristics completes the paper, which was presented before the Refinery Engineering Conference, Oil-World Exposition, Houston, Texas, October 15, 1937.

THE superior results obtained with the modern selective cracking unit are due to many refinements in design, among which the most basic is the segregation of cracking stocks according to both refractivity and boiling range. The general principles involved have been discussed in a previous paper.[1] These selected stocks are cracked under closely controlled conditions which result in optimum yield efficiency. The principles and practice of selective cracking have been developed over a period of years by a number of equipment and refining organizations. It is the purpose of this paper to describe a successful selective combination unit which has recently

[1] Combination Selective Cracking—E. R. Smoley, V. Mekler and A. H. Schutte—The Refiner and Natural Gasoline Manufacturer, June, 1937.

been put into operation and to outline the major plant operating conditions and overall performance.

The subject plant is a modern combination unit, employing three cracking heaters. It was designed to process 14,000 barrels per day of Van Zandt crude and has also processed East Texas and mixed Coastal crudes. The capital investment represented by a unit of this size makes it imperative that there be a minimum delay in getting the plant into productive operation. It is therefore of interest to note that the finished unit was delivered within 10 months after signing the contract. Two months later the unit was accepted. Upon the initial firing a 32-day run was made under acceptance test conditions before shutting down to allow the usual mechanical inspection for new equipment.

The process flow for this unit is shown in Figure 1. The crude charge receives preheat from the bubble tower trap tray reflux, quench, and gas-oil reflux streams before being passed through a separately-fired crude heater. From the crude heater the feed enters the topping tower where virgin naphtha is taken overhead, Stoddard solvent, reformer charge, kerosine and virgin gas oil as side streams, and reduced crude bottoms. The reduced crude blends with heavy cycle stock by direct contact in the upper section of the fuel oil flash tower where it acts as reflux. The vis-breaker charge is taken from a total drawoff deck in the central section of this tower.

Since a kerosine cut is made on the crude tower and there is a relatively small percentage of lower-boiling virgin gas oil in the crude, the segregation of the total gas oil cracking stocks into a light and heavy circulating stream is not economical in this case. There is, therefore, only one gas oil coil. In order to keep the charging stock for this coil clean, the boiling range is narrowed by operating the evaporator and fuel oil flash tower so as to include the heavy ends in the viscosity breaker charge. The gas oil heater operates at 940 to 990°F. temperature (depending on the crude charged) and 500 pounds outlet pressure; the vis-breaker at 880 to 885°F. and 240 pounds. In addition to the above two heaters there is a reformer heater which may also be operated as a once-through virgin gas oil coil. This coil usually operates at 940°F. and 750 pounds pressure.

The advantage of selective cracking of segregated charging stocks can only be realized when each stock is cracked under carefully controlled conditions of temperature and soaking time. With the conventional type

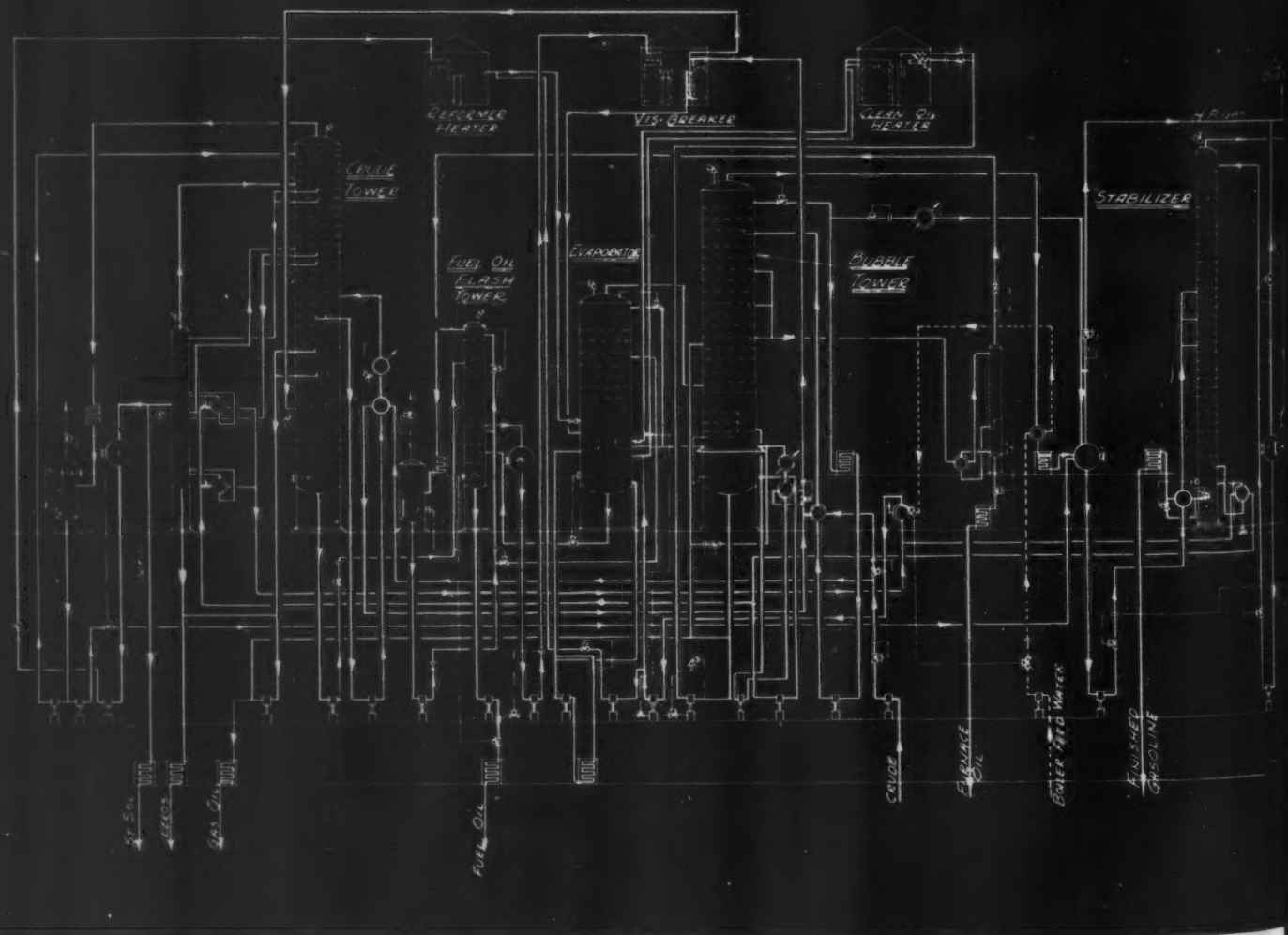


FIGURE 1
Process Flow Diagram.

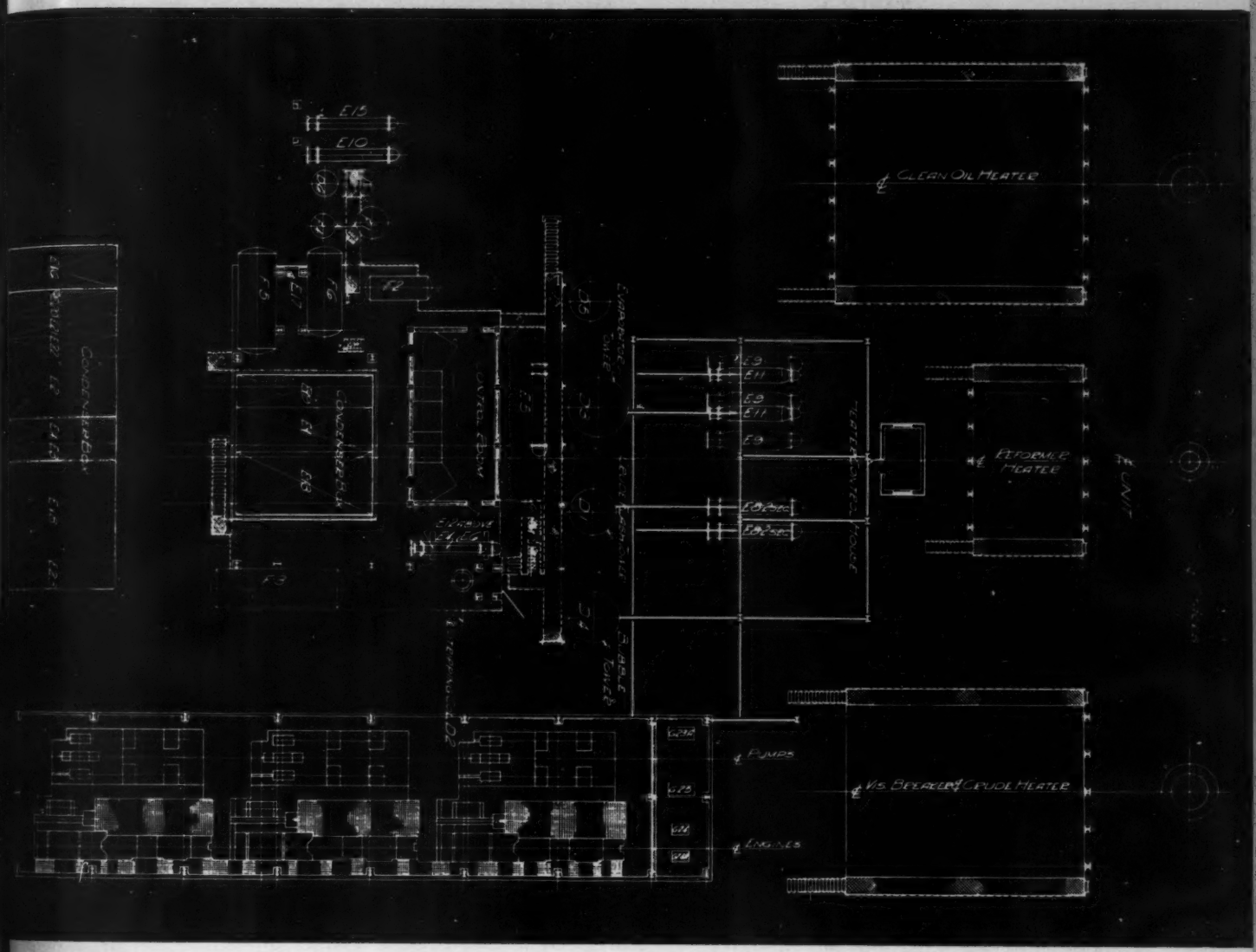


FIGURE 2

Plot plant showing general arrangement of items of equipment.

of heater the time allowed for cracking is fixed by the existing surface and the maximum transfer temperature which can be maintained without excessive coke formation. Particularly in the case of a unit of the type described, where many different crudes must be run, it is virtually impossible to design for optimum cracking conditions for each stock without providing independent control of the heating and soaking conditions. This is done by providing separately fired heating and soaking chambers in the furnace settings. This arrangement has been successfully used in a number of cases and provides an unusual degree of operating flexibility. In order that the heaters may operate with a maximum freedom from coke formation and with a satisfactory degree of temperature control in all parts of the preheating and soaking sections, it is important that the rate of heat transfer to the tubes be kept as uniform as possible. These conditions are obtained by a proper correlation between the flow of oil through the tubes, the flow of combustion products from the heating chamber and the disposition of tube surfaces. A typical heater arrangement is shown in Figure 3. Narrow, restricted areas through which the hot flue gases must pass usually result in eddy currents, channeling, dead corners and hot spots. The method of handling the combustion products which has been most successful is to remove them over the entire area of the roof. In the type of heater used on the unit which is being described the upper row of roof tubes is covered by special baffle tiles which give a restricted clearance between tube and tile, and therefore, a high gas velocity over the tube surface. This results in much higher convection transfer rates for the upper roof tubes and thereby makes the total transfer rates uniform for all tubes in the radiant section. A diagram of this baffle tile arrangement is shown in Figure 4.

Reference to the plot plan, Figure 2, will show the general arrangement of the items of equipment. The towers are symetrically grouped for maximum operating convenience and minimum piping runs. The hot and cold oil pumps are separated. All suction and discharge lines are overhead, leaving the pumphouse floor free from obstructions. The control house is centrally located above the pumphouse, giving the operators a general view of the plant and easy access to control valves and vessels where operating levels must be maintained.

Tables 1 to 7 summarize the operating conditions,

TABLE 1

Crude Inspections—Topping Operations

KEY:

Operation One—Cracking Van Zandt Crude—Reforming Heavy Virgin Naphtha.

Operation Two—Cracking East Texas Crude—Reformer used for once-through gas oil cracking.

Operation Three—Cracking Mixed Gulf Coast Crudes (Chiefly Bosco and Clarkwood)—Reforming Heavy Virgin Naphtha.

CRUDE INSPECTIONS.....	I	II	III
Crude	Van Zandt	East Texas	Mixed Gulf Coast
Gravity, ° A.P.I.	32.4	38.3	30.1
I.B.P.	180	90	240
5% at ° F.	224	105	335
10	262	155	385
15	304	208	421
20	350	260	448
25	400	309	470
30	444	360	492
35	484	408	508
40	524	459	524
45	564	508	542
50	610	558	560
55	656	610	580
60	686	660	600
65	...	712	635
70	...	...	670
75	...	...	682
80	...	...	714
Topping Operation			
Virgin Gasoline:			
Volume percent on crude	20.0	25.5	15.0
E. P. ° F.	354	342	390
O. N., C. F. R., A. S. T. M.	56.6	63.8	60.0
Gravity, ° A.P.I.	67.3	63.9	52.6
5% ° F.	141	133	168
Virgin Naphtha:			
Volume percent on crude	16.2	None	26.8
Gravity, ° A.P.I.	46.5	None	35.1
5% ° F.	363	None	423
E. P. ° F.	501	None	539
Stoddard Solvent:			
Volume percent on crude	None	8.5	None
Gravity, ° A.P.I.	None	47.8	None
I. B. P. ° F.	None	305	None
E. P. ° F.	None	406	None
Kerosine:			
Volume percent on crude	None	8.1	None
Gravity, ° A.P.I.	None	41.1	None
I. B. P. ° F.	None	380	None
E. P. ° F.	None	503	None
Virgin Gas Oil:			
Volume percent on crude	13.3	13.8	23.2
Gravity, ° A.P.I.	34.9	37.1	31.4
5% ° F.	460	450	514
E. P. ° F.	704	632	648
Color, N. P. A.	1	1	1½
Reduced Crude:			
Volume percent on crude	50.5	44.1	35.0
Gravity, ° A.P.I.	19.6	24.3	26.7

TABLE 2

Crude Charge and Heater Data

KEY: Same as Table 1

Crude	I Van Zandt	II East Texas	III Mixed Gulf Coast
Crude Charge Rate, B/D	**11,575**	**14,384**	**8,947**
Viscosity Breaker Heater:			
Throughput, B/D	10,800	10,800	10,260
Feed Gravity, ° A.P.I.	18.2	21.3	19.3
Inlet temperature, ° F.	610	620	575
Outlet temperature, ° F.	880	885	905
Outlet pressure, lbs. per sq. in.	240	240	240
Clean Oil Heater:			
Throughput, B/D	19,840	20,370	25,750
Feed:			
Gravity, ° A.P.I.	25.5	26.0	19.4
50 percent at ° F.	506	508	499
90 percent at ° F.	632	645	595
E. P. at ° F.	674	676	636
Color, N. P. A.	2½+	1½+	2½
Inlet temperature, ° F.	700	705	725
Outlet temperature, ° F.	980	940	990
Outlet pressure, lbs. per sq. in.	500	500	500
Reformer or Once-Through Virgin G. O. Heater:			
Throughput, B/D	1,870	1,915	2,400
Feed:			
Gravity, ° A.P.I.	46.5	37.1	35.1
50 percent at ° F.	419	532	469
90 percent at ° F.	472	596	512
E. P. at ° F.	501	632	539
Inlet temperature, ° F.	435	250	455
Outlet temperature, ° F.	940	940	965
Outlet pressure, lbs. per sq. in.	750	750	750

yields, product inspections and fuel economy when running Van Zandt, East Texas and mixed Coastal crudes. With regard to fuel economy it should be noted that the heater charge pumps are gas engine driven. Waste heat from the unit is used for steam generation in shell and tube units wherever the temperature level justifies it. Table 6 shows a steam production of 252,000 to 535,000 pounds per day.

The tabulated run data will be discussed in detail for each crude charging stock in the following sections. The yields, product quality, overall fuel efficiency and heater efficiencies which were obtained during the plant tests, demonstrate the satisfactory operation of this unit under varying charge stock conditions which demanded an unusual degree of flexibility. The different crudes were processed during the same run with a minimum of time required for adjusting plant conditions. The design basis for the unit was 14,000 barrels daily of Van Zandt crude when making kerosine and 11,000 barrels daily of this crude when cracking to ultimate yields.

OPERATION ONE

Operation one was on 32.4° A.P.I. Van Zandt crude with a charge rate of 11,575 barrels daily. A heavy virgin naphtha of 46.5° A.P.I. gravity and 501°F. end point was cracked once-through in the reformer heater. The quantity of this material was 16.2 percent by volume on the crude or a total of 1870 barrels daily. This charge was cracked under the mild conditions of 940°F. and 750 pounds per square inch pressure at the heater outlet. These conditions gave satisfactory octane number on the overall stabilized gasoline with optimum yields.

The virgin gas oil was pumped directly to the high pressure bubble tower and blended with recycle feed to the clean oil heater. The quantity of virgin gas oil was 13.3 percent of the crude charge or 1540 barrels daily. The total clean oil heater charge was 19,840 barrels daily. This 25.5° A.P.I. stock was cracked at 980°F. and 500 pounds per square inch pressure.

A 50.5 percent topped crude of 19.6° A.P.I. was withdrawn from the bottom of the crude tower and pumped through steam generators into the upper section of the fuel oil flash tower. Here it served as reflux

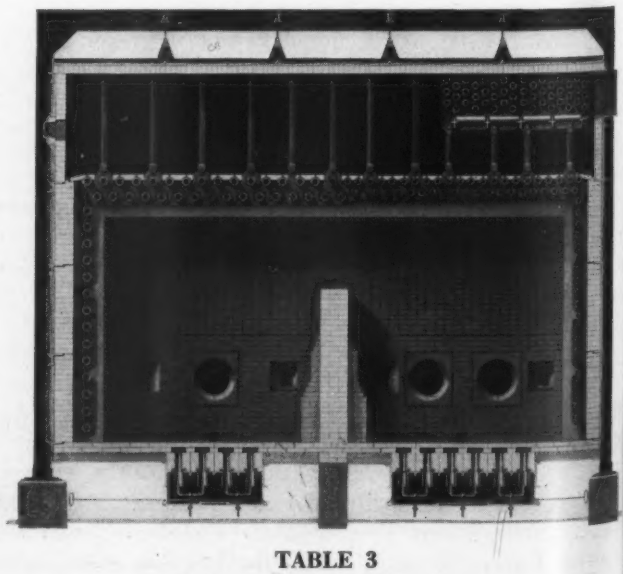


TABLE 3

Typical Heater Arrangement.

and combined with the heavy recycle stock flashed from the fuel oil in the lower section of this tower. This 18.2° A.P.I. gravity combined stock, amounting to 10,800 barrels daily, was charged to the viscosity breaker heater which was operated with a furnace outlet temperature of 880°F. and 240 pounds per square inch pressure.

The top of the fuel oil flash tower was refluxed with the overhead distillate to maintain a temperature of 480°F. thereby controlling the quality and quantity of

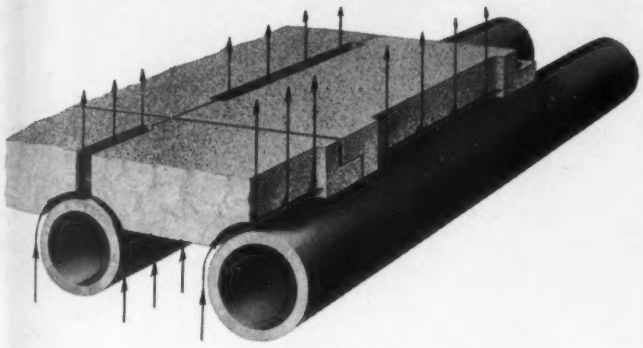


FIGURE 4
Baffle Tile Arrangement

the viscosity breaker feed. The excess flash tower distillate was pumped to the high pressure bubble tower where it served as reflux and was fractionated into clean oil heater charge and gasoline. The evaporator was maintained at 220 pounds pressure, 770°F. top, 815° bottom and 820° flash zone; the fuel oil flash tower at 5 pounds pressure and 705° bottom temperature. Under these conditions a 7.5° A.P.I. gravity final fuel oil was obtained which had a 290 Furol viscosity at 122°F. and 35°F. pour.

The unstabilized gasoline from the bubble tower was mixed with the straight-run gasoline from the crude tower and the whole quantity stabilized in a fractionating column which was run as an integral part of the unit. This stabilization produced a 7.8-pound Reid finished gasoline bottoms and gas overhead.

The operation gave a total overall yield of 62 percent by volume on the crude charge of 7.8-pound Reid vapor pressure, 65 octane number gasoline, a 29.1 percent yield of Bunker "C" specification fuel oil and 10 percent gas.

OPERATION TWO

During the second operation East Texas crude of 38.3° A.P.I. gravity was processed into the products shown in Table 4, that is, gasoline, Stoddard solvent, kerosine, fuel oil and gas. The crude charge rate was 14,384 barrels daily. The reformer was used as a once-through gas oil coil since all of the naphtha and kerosine were taken out as finished products. A 25.5 percent cut

TABLE 6
Utilities
KEY: Same as Table 1

Crude	I Van Zandt	II East Texas	III Mixed Gulf Coast
*Fuel consumption, percent crude charge	5.93	5.56	6.79
Steam produced, lbs per day of 150 lbs. steam	446,000	252,400	534,900
Steam consumed, lbs. per day	441,000	445,900	462,000
Net steam consumed	None	193,500	None

* Fuel to the heaters, as equivalent bunker "C" fuel oil.

TABLE 3
Fractionating Equipment
KEY: Same as Table 1

Crude	I Van Zandt	II East Texas	III Mixed Gulf Coast
Crude Tower:			
Operating pressure, lbs. per sq. in.	20	15	9
Top temperature, ° F.	290	270	320
Naphtha drawoff, ° F.	440	370	475
Kerosine drawoff, ° F.	...	445	...
Gas/Oil drawoff, ° F.	600	550	595
Flash zone, ° F.	700	650	675
Fuel Oil Flash Tower:			
Operating pressure, lbs. per sq. in.	5	6	8
Top temperature, ° F.	480	485	430
Viscosity breaker charge draw-off ° F.	610	615	575
Bottom temperature, ° F.	705	715	695
Evaporator Tower:			
Operating pressure, lbs. per sq. in.	220	220	215
Top temperature, ° F.	770	785	765
Flash zone, ° F.	820	835	820
Bottom temperature, ° F.	815	810	805
Bubble Tower:			
Operating pressure, lbs. per sq. in.	215	215	210
Top temperature, ° F.	435	425	420
Middle temperature, ° F.	560	540	655
Bottom temperature, ° F.	710	705	735
Trap tray reflux out of Tower, ° F.	480	460	430
Trap tray reflux into tower, ° F.	125	185	125
Stabilizer Tower:			
Operating pressure, lbs. per sq. in.	250	275	270
Top temperature, ° F.	155	145	170
Feed temperature, ° F.	315	335	330
Bottom temperature, ° F.	425	425	440

TABLE 4
Yields and Product Inspections
KEY: Same as Table 1

Crude	I Van Zandt	II East Texas	III Mixed Gulf Coast
Yields (Volume % on crude):			
Stabilized gasoline	62.0	55.5	64.7
Stoddard solvent	...	8.5	...
Kerosine	...	8.1	...
Fuel oil	29.1	23.2	23.8
Gas and loss	10.0	6.1	12.5
Stabilized Gasoline:			
O N., C. F. R., A. S. T. M.	65.1	65.8	71.2
Gravity, ° A.P.I.	62.2	60.8	54.8
I. B. P., ° F.	99	96	99
10 percent at ° F.	140	137	139
50 percent at ° F.	241	245	264
90 percent at ° F.	348	350	368
E. P. ° F.	402	401	394
Reid vapor pressure	7.8	8.6	8.2
Color, untreated, Saybolt	+21	+23	+22
Gum, untreated, cubic dish, mg/ 100 cc	13.7	9.8	14.6
Fuel Oil:			
Gravity	7.5	10.0	7.0
Viscosity, furol at 122° F.	290	130	86
B. S. & W.	0.2	0.3	0.1
Sediment, percent	0.072	0.149	0.046
Pour, maximum	35	20	30
Flash, P. M., ° F.	230	210	230

TABLE 5
Flue Gas Analyses and Heater Efficiencies
Flue Gases

Heaters	Percent Efficiency	ANALYSIS CO_2	ANALYSIS O_2	Draft in Inches
Viscosity breaker and crude oil.	72.3	....	....	....
South side	....	9.0	5.7	.36
South side center	....	8.5	7.7	.44
North side center	....	9.4	5.8	.40
North side	....	9.5	6.1	.37
Stack (final breeching)	....	8.9	6.9	.49
Reformer	72.1	....	....	....
South side	....	8.6	7.6	.10
South side center	....	10.6	4.6	.10
North side center	....	11.0	4.1	.10
North side	....	....	....	.10
Stack (final breeching)	....	10.5	4.0	.47
Clean Oil	75.4	....	....	....
South side	....	11.2	3.0	.27
South side center	....	11.8	2.2	.35
Center	....	12.0	1.7	.39
North side center	....	11.1	2.7	.37
North side	....	10.4	4.2	.37
Stack (final breeching)	....	11.0	3.4	.53

Gas Engine-Driven Hot-Oil Pumps in combination selective cracking process

of 342 end point straight run gasoline was taken overhead from the crude tower. The rest of the operation was essentially the same as in operation one except for temperatures and throughputs on the different cracking coils.

The once-through gas oil coil was operated with an outlet temperature of 940°F. and a pressure of 750 pounds per square inch. The charge rate was 1915 barrels daily or 13.8 percent by volume of crude charge of a 37.1° A.P.I., 632 end point stock. The low coil inlet temperature of 250°F. was due to the fact that the virgin gas oil passd through a crude exchanger before going to the feed accumulator.

The clean oil coil was maintained at 940°F. outlet and 500 pounds per square inch pressure. The charge to this coil was 20,370 barrels daily of a 26.0° A.P.I., 676 end point stock having a 1½ + N.P.A. color. Due to taking virgin products from the crude tower and once-through cracking the virgin gas oil there was very little virgin feed stock to the clean oil coil. This coil could be operated at a high recycle ratio under mild conditions to enhance the yields, while still meeting octane requirements.

Operating conditions maintained on the vis-breaker coil outlet were 885°F. and a pressure of 240 pounds per square inch. As in operation one the composition of the vis-breaker charge stock was approximately a 1:1 ratio of heavy recycle and virgin reduced crude. The characteristics of the charge for this operation were 21.3° A.P.I. gravity, 495°F. initial and 50 percent at 688°F. The charge rate to this coil was 10,800 barrels daily.

This operation gave very satisfactory results from every viewpoint. A 55.5 percent yield of 400°F. end point finished stabilized gasoline of 65.8 octane, 8.6 pounds. Reid vapor pressure was obtained while making 8.5 percent Stoddard solvent of 305 initial boiling point to 406 end point and 8.1 percent finished kerosine with a boiling range of 380 to 503°F. This is equivalent to 70 percent gasoline when running to ultimate yields. The fuel oil had a 10.0° A.P.I. gravity and 130 viscosity Furol at 122°F. It is interesting to note that there was only a 6.1 percent gas yield from this operation.

OPERATION THREE

When the unit was swung from the East Texas crude operation previously described to mixed Gulf Coast crudes a careful and quick manipulation of operating conditions had to be made because these charge stocks are very dissimilar in characteristics. East Texas crude contains 34 percent of 400 end point gasoline but mixed Gulf Coast has about 15 percent. The mixed Gulf Coast charge, which was preponderantly Bosco and Clarkwood, had a large percentage cut boiling between 400°F. and 700°F., and a proportionately smaller amount of reduced crude. Despite this difference in charge stocks, the unit was lined out without delay and the crude throughput capacity and operating levels rapidly established.

From this charge stock the straight-run products were 15.0 percent gasoline, 26.8 percent reformer charge, 23.2 percent gas oil and 35.0 percent reduced crude, from a crude charge of 8947 barrels daily. The reformer was maintained at the same conditions as for the previous operations and charged with 2400 barrels daily of a 35.1° A.P.I. stock which had a boiling range of 423 to 539°F.

The lower crude throughput capacity reflects the higher percentage of intermediate boiling range virgin gas oil and the greater refractivity of the clean oil charge obtained from these Coastal crudes. The clean oil coil therefore operated at a higher charge rate, 25,750 barrels daily, and the outlet temperature was raised to 990°F. In this case the clean oil charge was 19.4° A.P.I., 50 percent at 499°F. and 636 end point. This low end point was obtained by running a lower temperature on the top of the evaporator and fuel oil flash tower, thus increasing the vis-breaker charge. This flexibility allowed a better balance of heater duties. The vis-breaker charge was 10,260 barrels daily or nearly the same as for the Van Zandt and East Texas operations. Due to the refractory nature of the stock this coil operated at 905°F. and a ratio of virgin reduced crude to recycle stock of 1 to 2.3. These conditions may be compared with 885°F. outlet temperature and 1 to 1 recycle ratio for the Van Zandt operation.

The overall yields obtained on the mixed Gulf Coast charge stock were 64.7 percent stabilized gasoline, 23.8 percent fuel oil and 12.5 percent gas. The gasoline was 71.2 octane number, 8.2 Reid vapor pressure; the fuel oil 7.0° A.P.I., 86 Furol vis at 122°F., 30°F. pour and 0.1 percent B.S.

GENERAL COMPARISON OF OPERATIONS

The data presented for the three operations described above permits an interesting comparison to be made of the operating conditions for this unit when processing crudes of rather widely different character. The clean oil heater throughput is seen to increase with the refractivity of the stock, and the crude capacity to decrease, allowing of course for the higher crude rate obtained on East Texas due to taking off straight-run products.

The octane and end point of the virgin naphtha cut taken while running Van Zandt was set by the optimum conditions for overall octane-yield relationship. On East Texas crude the end point and octane of this virgin cut were fixed by the cut point of the Stoddard solvent taken as a product. In the case of the mixed Coastal charge, a 400 end point virgin gasoline was taken since the more refractory cracking stocks naturally gave a higher overall octane number when processed under conditions sufficiently severe to give optimum yields.

Table 5 shows the flue gas analyses taken on the three heaters during Operation Three, the draft gauge readings and the calculated heater efficiencies. These tests were made under normal plant running conditions and demonstrate the high degree of heat economy obtained with the type of heater described in the introductory section of this paper.

The equivalent fuel to the heaters, expressed as volume percent fuel oil on the crude charge, is given in Table 6. These ranged from 5.56 to 6.79 percent depending on the type of charge stock and the cracking temperatures and circulation rates required. As previously mentioned, the waste heat from this unit is used to produce steam wherever economically justifiable. The steam production and consumption figures are also given in this table. It will be noted that there was a net steam production for two of the operations.

The atmospheric distillations of the crudes, given in Table 1, show weathering of the sample on Van Zandt and mixed Gulf Coast.

The overall yields were obtained by tank gauges under acceptance test run conditions. The gas loss on the topping operation is included in the overall gas and loss.

Operating control board in modern combination selective cracking process

Metallurgy of Petroleum Refining Equipment

E. S. DIXON
Metallurgist, The Texas Company

MOST of the large oil companies are well informed metallurgically, either through metallurgical laboratories of their own or through the knowledge gained by engineers and designers who have access to the published work on the subject of metallurgical requirements in oil refineries.

VARIOUS publications present this subject admirably but undoubtedly many refiners do not read the information which is available. I shall abstract certain information, and will present such new information as I may have. It is my thought to give definite information not available in the literature, which will be taken from the files and practice of The Texas Company, for example, under corrosion, our method of lining towers has a definite technique; the cost of so doing, protection obtained, methods of inspecting, training men, etc., are all a part of our records.

These and other actual experiences are valuable when incorporated in a paper for operating and maintenance executives to read.

The modern petroleum refinery demands much of equipment which has changed rapidly in relatively few years from the simple units of early petroleum refining to the modern ones of today.

The operating personnel must be protected by proper materials and proper inspection; therefore, the refiner looks to the metallurgist for guidance.

This paper was presented before the Refinery Engineering Conference, Oil-World Exposition, Houston, Texas, October 15, 1937.

MATERIALS OF CONSTRUCTION

Refinery equipment subject to corrosion may be divided into several classes:

Pressure Stills
Pipe Stills
Treating Equipment
Tanks, transfer lines and equipment subjected to atmospheric corrosion.

Steel is the principal metal used for refinery construction. Brass, bronze, monel, aluminum, cast iron, lead, stainless steel and other metals find their place in refinery construction.

In pressure still service the metal must have strength to operate under temperature and pressure, and it must resist corrosion. In recent years there has been an increased use of alloys for pressure still service.

In pressure stilling equipment, safety of the vessels is of prime importance. Because of their size and the large amount of oil which they contain, failure results in loss of life and property.

Pressure vessels are usually made of carbon steel of the boiler steel class. The American Society for Testing Materials has a specification covering this steel. All of the reliable still manufacturers are exacting in the kind of steel entering their vessels.

Pressure vessels are usually fabricated by electric welding. Great advances have been made in the last few years in electric welding construction of pressure vessels. Improved welding technique with covered rods, the use of stress relieving in huge furnaces, the inspection by the X-ray, are procedures used by the modern pressure vessel manufacturer. Pressure vessels are built with elliptical heads; manways and other openings are reinforced and every effort is made to design them 100 percent. Some refiners operate vessels of older manufacture. It is well for them to appraise their vessels, making due allowances by means of approved factors of safety for such vessels.

Because of the high temperatures and high pressures under which these units operate, great care is used in the selection of metals. With few exceptions, low carbon steel is used for pressure vessel construction. Initial cost, workability, reliability and availability are the factors which determine this selection. It has been customary to use low carbon steel in construction of boilers, and its selection is correct for moderate temperature where corrosion is not serious. The physical properties of low carbon steel under such conditions are adequate. This material in common with all other ferrous alloys suffers a loss in tensile strength when subjected to temperatures in excess of about 700°F. (See Figure 1) and this loss becomes increasingly greater the higher the temperature. This is a phenomenon known as creep or plastic deformation under high temperature conditions at relatively low stress values. If a material is subjected to a stress in excess of the critical value, the rate of deformation becomes rapid and in the course of time rupture occurs. It is therefore necessary to design and operate vessels intended for high temperature and pressure so that this limiting creep stress will not be exceeded. Low carbon steel corrodes rapidly in oil cracking service and unless vessels are protected by some means, such as liners or use of neutralizers the limiting creep stress will in time be exceeded and the vessel must be operated at lower pressure or it must be discarded. The problem of selecting safe unit stresses, therefore, resolves itself into one of first determining a safe allowance for creep and then finding the stresses corresponding thereto. Rate of creep for pressure vessels operating at The Texas Company plants must not

exceed 1 percent elongation in 10,000 hours. The following table shows values used:

0.24 Percent Carbon Steel

Temperature	Short Time Ultimate Strength	Stress Producing Not Over 1 Percent Creep in 10,000 Hours
Up to 732	56,000	12,500
800	49,500	10,000
820	47,750	9,250
890	41,500	7,250
1000	31,250	4,625
1100	23,500	2,750

Figure 1 shows these values plotted.

Figure 2, Curve 3, is an enlargement of Figure 1, Curve 2.

There are many published data and considerable disagreement one laboratory with another; we feel the values used are conservative. There are many reasons advanced for discrepancies in Load-Carrying Abilities of carbon steels. It is felt that manufacturing variables have an effect on the creep resistance of steels and there is a research project of the Joint Research Committee of the A.S.T.M.-A.S.M.E. on Effect of Temperature on the Properties of Metals dealing with this problem.

After the allowable unit stress is evaluated it is used in the well known Barlow formula for cylindrical vessels.

$$T = \frac{PR}{CS}$$

T = Thickness of metal in inches.
P = Allowable operating pressure, lbs. per sq. in.
C = Constant for design.
S = Allowable unit tensile stress, lbs. per sq. in.
R = Nominal Radius of shell in inches.

This formula can be rewritten as $P = \frac{TCS}{R}$

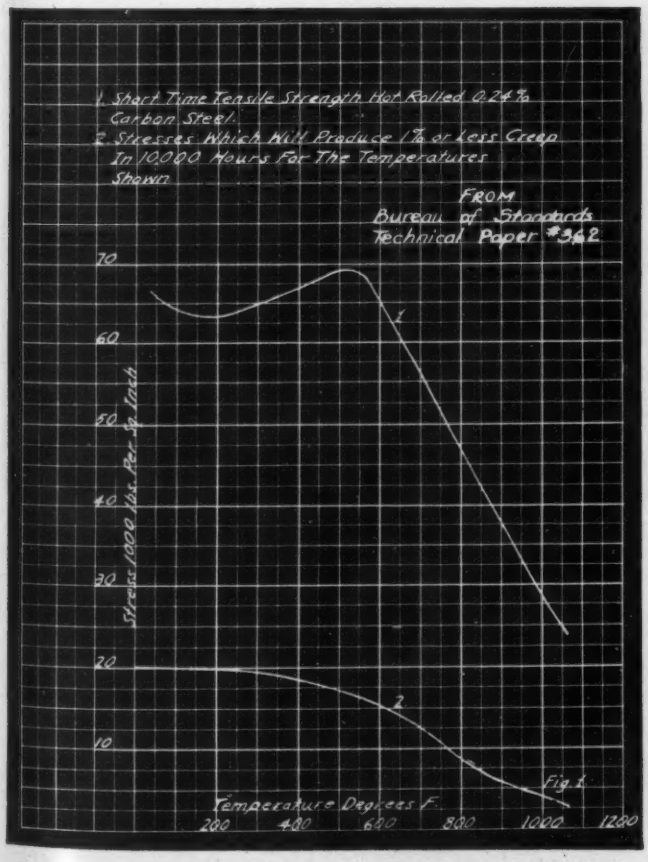

1. Short Time Tensile Strength Hot Rolled 0.24% Carbon Steel.
2. Stresses Which Will Produce 1% or Less Creep In 10,000 Hours For The Temperatures Shown
FROM Bureau of Standards Technical Paper #362
Stress 1000 lbs. Per Sq. Inch
Temperature Degrees F.
200 400 600 800 1000 1200
Fig. 1

FIGURE 1

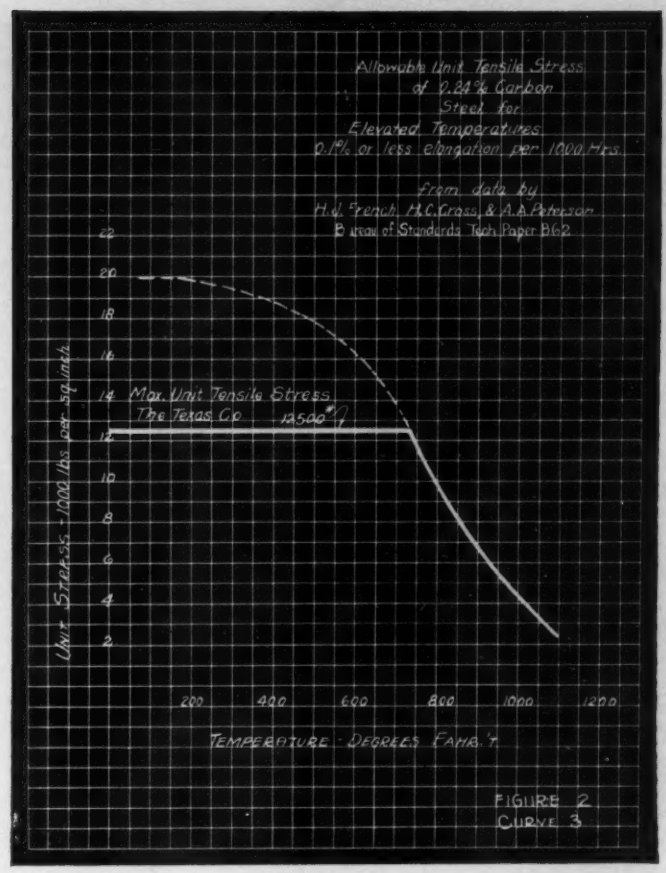

Allowable Unit Tensile Stress of 0.24% Carbon Steel for Elevated Temperatures 0.1% or less elongation per 1000 Hrs.
From data by H.J. French, H.C. Cross, & A.A. Peterson Bureau of Standards Tech Paper B62
Max. Unit Tensile Stress The Texas Co 12500#
Unit Stress - 1000 lbs per sq inch
Temperature - Degrees Fahr.°F
FIGURE 2 CURVE 3

FIGURE 2

It is not the purpose of this paper to discuss Barlow's formula. Much has been done by manufacturers of pressure stills to keep the constant for design as nearly 100 percent as possible. Reinforced manways and reinforced openings, elliptical heads, stress relieving in huge furnaces, X-ray inspection, etc., are much discussed problems. The metallurgist must supply a metal with high allowable stress under operating temperature. He must supply steel which will resist corrosion.

In the formula, "T" must not decrease because of corrosion, "S" must have as high a value as possible. There are now on the market high strength steels worthy of consideration for this purpose. I know of no actual experience with them in cracking vessels, however.

USE OF LINERS

To prevent decrease in wall thickness we must reduce corrosion. This can be done in several ways. Some neutralizer of corrosion can be used, such as lime, soda ash or ammonia. All three have been used. This problem is for the chemist and operator.

Many vessels are lined with non-metallic liners or with metal liners. The liner selected depends on the cost and rate of corrosion. Metallic liners are of two classes: First, sheet metal, usually stainless steel, appropriately bonded into place; and, Second, sprayed liners which for pressure stills are usually aluminum or 18-8. The bonded stainless steel sheet gives 100 percent protection. Certain kinds of stainless steel when used for liners, crack (see Photo 18617), but continue to give protection. It is claimed that changing the analysis will prevent cracking. These liners are costly but since they give complete protection, the walls of the vessel can be made

PHOTO 18,617

thinner; no allowance for corrosion is necessary as is the case with carbon steel.

Sprayed liners give protection for a definite period. I know of some liners where protection is good for two years. Then the vessel must be sprayed again. This is also a costly procedure. The first cost per square foot is approximately $1.25 for aluminum with the refinery supplying some of the common labor for initial cleaning, scaffolding, etc. Some users of sprayed coatings report them as being unsatisfactory. It depends on who does the job.

The most serviceable and most economical liner is gunite which is a 1:3 cement-sand mixture. It is used quite universally, but there are some locations where it is not applicable. I refer particularly to chambers where coke is removed mechanically by heavy metal weights revolving and beating out coke deposits.

Gunite is applied 1 to 1½ inches thick over the vessel walls by means of a "cement gun." Gunite is in reality reinforced concrete; the reinforcing consisting of wire mesh tied to ¼-inch rods which are welded to the shell. The finished concrete liner is given a steam pressure cure for 24 hours after which it is ready for use. Application of gunite for liners is an art gained only through

experience. Men skilled in applying gunite in unrestricted quarters or in the open are unable, as a general rule, to shoot, successfully, gunite liners in vessels. The exact trick—if you would call it that—has never been determined. Directions as furnished with the "Cement Gun" must be followed to the letter. There must be no overlapping of work, work must be continuous and of one layer only, otherwise trouble results.

The cost of such liners depends on the location of refineries, including removal, varies from $0.40 to $0.70 per square foot of surface.

This same material is also used with success in lining tanks, particularly in the bottoms, which stand partially filled with water. The usual life of such a liner is upwards from three years. How much longer they will last, I do not know.

The mixtures used on all of this work consists of 1 part by volume of cement (Portland preferred) to 2½ or 3½ parts of well graded sand. Clean, pure water is used, being applied to the sand-cement mixture at the nozzle to give a relatively dry mix.

Figure 3 shows actual protection afforded pressure vessels. Values are taken from records of wall thickness obtained by drilling and measuring (Refer to Figure 3). Prior to 1931 the average loss of metal in unlined vessels was approximately 1/16-inch per year. In 1931, due to changes in charge stock or changes in operation, the average yearly loss in metal thickness began to approach ¼-inch. These are average values. Some vessels corroded more rapidly and considerable concern was felt because it was readily seen that in the future, pressure must be reduced with ultimate early replacement of vessels. In 1932 protection by gunite was afforded as shown, and the life of a lined vessel is now indefinite nor will pressure be reduced because of decreased wall thickness.

Some vessels are brick lined because under certain conditions of operation gunite spalls. The pressure and temperature seem to be a factor with respect to success or failure of gunite. Brick lining is satisfactory in many places. Corrosion sometimes continues behind the brick, therefore it is necessary to use the proper binder and remove the brick yearly for inspection purposes. With the use of gunite and brick liners in unfired vessels, the steel operates at a lower temperature than the oil in the vessel and by referring to Figures 1 and 2 one will observe that the lower the temperature the higher are the allowable operating stresses. It is an advantage to keep the metal as cool as possible.

TUBING

The choice of tubing for furnaces and hot lines in pressure stills is of importance. Seamless tubing is standard for these services.

There are several characteristics which must be remembered in the selection of tubing.

Corrosion resistance: Metal must be resistant to hydrogen sulphide, which attacks carbon steel rapidly at temperatures above 600°F. Where corrosion is the result of mineral or other acids, it is customary to neutralize with lime, ammonia or some other agent.

High-Temperature Strength: This is an essential property, as discussed with regards to vessels, above.

Stability of properties: The requirements are that metal must not become brittle or weakened in service because of change in structure. For example; 18-8 is not recommended for service above 1200°F. because of lack of stability. We are told that the 18-8 tubes manufactured today are of a better analysis. The carbon is kept lower than was the case with the earlier tubes. Additions of Titanium or Columbian are claimed to reduce failure from lack of stability. The original 4-6 percent chrome tubes became brittle when cold and many cases are on record where these tubes fractured during the cleaning (knocking) operation. These tubes are extremely tough at operating temperatures (300°F. or greater). The addition of 0.5 percent molybdenum to this analysis has increased its stability and toughness when cold and no cases are on record of brittle failures of this alloy.

Indications of impending failures: When a tube becomes overheated, it is desirable that it swell gradually so that the operator can be forewarned and shut down the unit prior to failure. The 4-6 percent chrome is excellent in this respect. Many instances of swelling of this alloy are on record. It is not unusual to have the I.D. of the swell portion much greater than the normal original O.D. of the tube, without rupture occurring.

Ease of Fabrication: Desirable qualities are weldability, cold and hot bending, flaring and flanging. 4-6 percent chrome is air hardening. Lines fabricated hot must be furnace annealed. All field welds must be annealed.

Thermal Expansion: Since carbon steel is widely used, the coefficient of expansion of alloys should be nearly that of mild steel.

Scaling resistance: The metal should not scale readily. The resistance of carbon steel to scaling decreases rapidly above 1150° F. 4-6 percent chrome is more resistant to scaling; it is probably usable at 1250° F., continuous operation. Above these temperatures some other alloy should be used, bearing in mind that in addition to scale

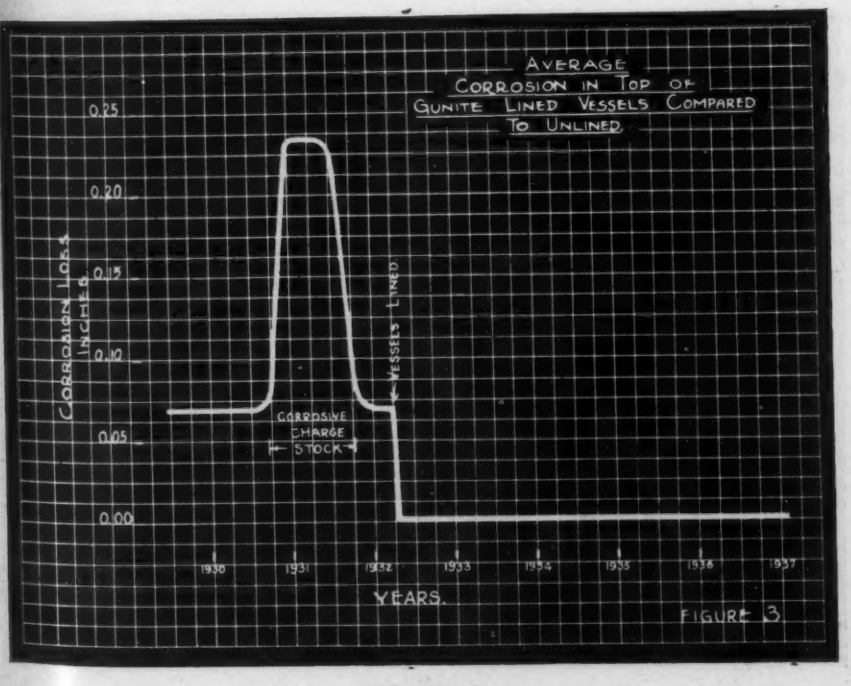


FIGURE 3

resisting properties the question of stability must be considered.

Cost: Since carbon steel is the lowest in price, any alloy to replace it must be fairly reasonable in price or the need for corrosion resisting metal must be great.

The above properties are not developed in any one metal. Carbon steel is deficient with respect to corrosion resistance and strength at high temperature; it scales rapidly.

18-8 is high in price, it cannot be heated in excess of a definite temperature because of brittleness; however it does not corrode, it does not scale readily, and it is strong at high temperatures. It has its place where needed and in the hands of informed operators it is successful.

4-6% chromium-molybdenum tubes are intermediate. They are too high in price for general use unless corrosion is severe. They are strong under temperature; and are good enough with respect to corrosion resistance in many refineries. At Port Arthur Works many 4-6% chrome tubes have a life to date of 8 years and some have a life of 9 years. The present loss in wall thickness indicates they will last, with respect to corrosion, 12 years, and they are fired continuously with a metal temperature of 1300° F. part of the time in each run. They do fail from swelling, and from distortion, but not from corrosion, and rarely from splitting.

Let us assume that a designer of equipment is called upon to select tubes for furnace and outside lines. If he is acquainted with the crude he must run, he can select his tubes readily. If the crude is sweet, carbon steel will be his choice. If he wishes to use a thin walled tube and demands higher strength, he may select carbon-molybdenum or some other steel which has high creep strength at elevated temperatures. These high creep strengths are usually the results of laboratory experimental work on selected alloys. The designer in using these values must feel assured that high creep values hold for steels in tubes fired for several years.

If the crude is corrosive the designer will use 4-6% chrome or some modification, depending upon the life he expects and the money he will spend. If corrosion is very severe and he wishes to pay the price, he may use 18-8 and watch it closely for lack of stability.

Some designers, not knowing the corrosion rates of the units to be built, specify carbon steel, granting that early replacements may be necessary. Then the alloy for replacements will be selected from experience with carbon steel. Some tubes may remain carbon, some become 4-6%, some 9% chrome. After a unit begins operation but before the behavior of the unit with respect to corrosion can be learned by drilling the lines, or when the charging stock is changed to a more corrosive oil, the method of using small corrosion specimens in various locations gives advance corrosion information. Many refineries use some method of this sort, and it is recommended that in refineries where corrosion rates per year are unknown and where selection of metals is largely by guess, some method of forecasting corrosion rates by laboratory samples be initiated. This work is explained later in the paper. The usual chemical laboratory personnel can do this work.

The following table gives an estimate of the life of 4-6% chrome compared to carbon steel. A similar table can be compiled for 2% chrome or 18-8.

Approximate Life of Tubes Subjected to High Temperature Sulphide Corrosion

Service	Life of Carbon Steel, Years	Life of 4-6 Percent Chrome, Years	Ratio
Mild	8	10	1.25:1
Moderate	2	8	4:1
Severe	½	3	6:1
Very severe	⅕	2	10:1

The cost in the above table is not considered. It depends on quantity purchased, etc. Reviewing this table, one will note that for mild service carbon steel is the correct tube to use, and many refineries will consider nothing else. For severe and very severe service some alloy steel is desirable. For moderate service it is largely a matter of decision on the part of refinery executives as to whether or not tubes which are replaced every 2 years should be 4-6% chrome. With a life of 2 years carbon steel is often sufficiently good; with a life of 1½ years, 4-6% chrome should be used; and between 1½ and 2 years, the plant management should decide.

Recently an entire series of chrome steels has been placed on the market. Selection includes 2% and 9% chrome so that it seems there is a tube for every part of each installation.

High Temperature Strength: Recently, the trend has been to higher temperatures and higher pressures and to longer battery runs. While these are serious factors in tube failures, most heaters can operate with carbon steel tubes, if strength is the only factor considered. Alloys are introduced primarily because of their resistance to corrosion, but we are glad also to take advantage of their resistance to stress at high temperature.

The question of creep is of much more importance with a pressure vessel than with a heater tube. The vessel is larger, its failure would be a calamity with loss of life. But heater tubes may be allowed occasion-

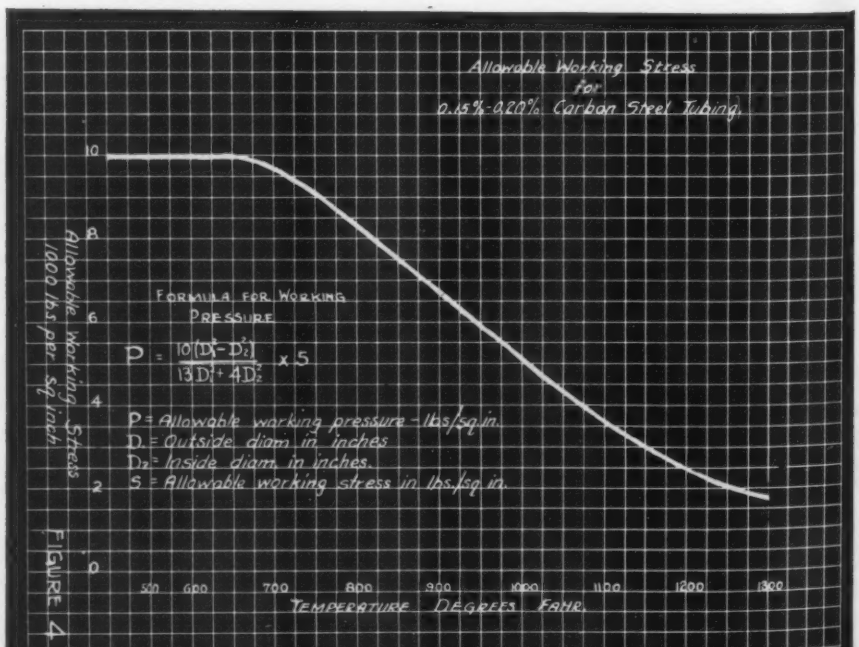


FIGURE 4

FIGURE 4

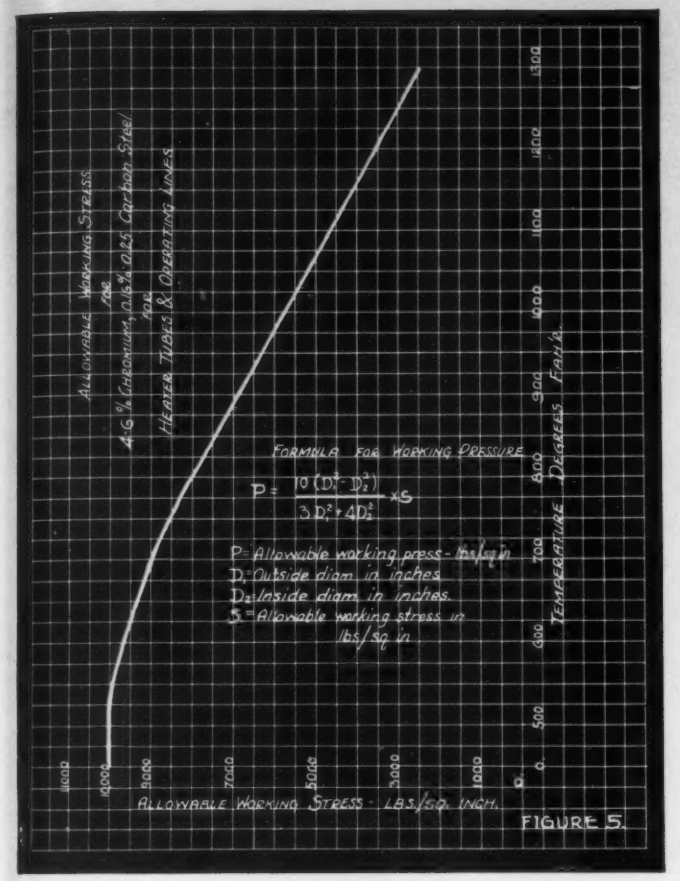

ALLOWABLE WORKING STRESS
FOR
4-6% CHROMIUM, 0.45% 0.25 CARBON STEEL
AND
HEATER TUBES & OPERATING LINES
FORMULA FOR WORKING PRESSURE
P = 10 (D₁² - D₂²) / 3D₁² + 4D₂² × S
P = Allowable working press - lbs/sq in
D₁ = Outside diam in inches
D₂ = Inside diam in inches
S = Allowable working stress in lbs/sq in
TEMPERATURE DEGREES FAHR.
ALLOWABLE WORKING STRESS - LBS/SQ. INCH.
FIGURE 5

FIGURE 5

ally to fail. Though failure is undesirable, seldom is anyone injured; the fire is enclosed in a furnace. Property damage is relatively low. Therefore, heater tubes are not operated with extreme conservative temperatures and creep values. They do creep; they swell; they occasionally rupture. This is particularly true of the older units of 8 or 9 years ago. Modern furnaces have fewer hot tubes. The first thought of the designer is this: The tube should not fail suddenly when it goes into operation, opening up at once with an explosive burst as it comes to temperature. This can be prevented by using a working stress obtained by dividing the ultimate strength of the metal at the high temperature by a generous factor of safety.

Objections can be raised against basing high temperature design on the ultimate tensile strength determined in a short time test; but from a practical point of view when the factor of safety is chosen properly to avoid excessive numbers of failures from bulged or split tubes, short time failures resulting from over-heated metal, then long time creep failure gives little or no trouble to the operator.

If the tube operates at a higher stress than an allowable creep stress of 1% in 10,000 hours, it will at the worst do no more than swell slowly during days and weeks of operation, and operators and inspectors will detect the swelling and remove the tube. In practice, bulging by creep, either long time or short time creep, is not found to be an expensive problem; failures and split tubes occasionally happen but these are found to be due to extra thick coke inside the tube or flame impingement. In these cases heavy scaling of the tubes is seen, and this indicates unusual and excessive temperature.

The writer assumes that it will be read by operators, many of whom have been in the business a long time so that they have developed excellent methods of their own for calculating the value of their various tubes.

For others, who are newer to the industry, a system is detailed below which is working well in practice.

Every hot tube under pressure must be appraised with respect to the pressure it can carry under the temperature at which it operates. The size of the tube and the wall thickness together with the kind of metal governs the allowable pressure at this temperature. The wall thickness decreases due to corrosion and erosion or wear; therefore it must always be known by systematic drilling and measuring or hammer testing.

The following formula has been used successfully in appraising tubes.

Formula:

$$P = S \times \frac{10(D_1^2 - D_2^2)}{13D_1^2 + 4D_2^2} \text{ (Clavarino's)}$$

P = Allowable pressure, p.s.i.
S = Allowable working stress at the temperature of operation, p.s.i.
D_1 = Inside diameter of tubing, inches.
D_2 = Outside diameter of tubing, inches.

Allowable Stress:

$$S = \frac{T.S.}{F.S.}$$

TS = Ultimate tensile strength, from short time test at high temperature.
Design values for 0.10-0.20 percent carbon steel and 4-6 percent chrome, and 18-8, are tabulated below.
Values are for material in a soft, ductile condition suitable for tubing.

Ultimate Tensile Strength

Temperature (Degrees)	Carbon Steel	4-6 Percent Chrome Note 1	18-8
0- 500	Use 60,000 p.s.i.	Use 60,000 p.s.i.	Use 90,000 p.s.i.
550	Use 60,000 p.s.i.	Use 59,520 p.s.i.	Use 90,000 p.s.i.
600	Use 60,000 p.s.i.	Use 58,500 p.s.i.	Use 90,000 p.s.i.
650	Use 60,000 p.s.i.	Use 56,760 p.s.i.	Use 90,000 p.s.i.
700	57,990	54,300	72,000
750	54,480	51,720	71,000
800	49,980	48,420	68,000
850	45,000	45,000	66,000
900	40,020	41,700	63,000
950	34,980	38,400	61,500
1000	30,000	35,040	60,000
1050	25,260	31,740	58,000
1100	21,240	28,320	56,000
1150	17,400	25,020	53,000
1200	14,220	21,720	49,000
1250	11,760	18,300	46,000
1300	10,020	15,000	41,000

NOTE 1: The tabulated values apply to plain 4-6 percent chrome. The addition of molybdenum or tungsten strengthens the steel as regards creep resistance, but not materially as regards the strength necessary to resist the type of temporary overloading which actually causes the majority of tube failures.

F.S.—The factor of safety. The value depends on the certitude with which safe operating stresses are derived by past experience, and with the reliance to be placed on the estimation of true metal temperatures, etc.

A value of 6 is suggested for use in cracking process heaters.

Some authorities recommend increasing the factor of safety at higher temperatures, and this step is recommended as in accordance with the trend developed by creep tests.

METAL TEMPERATURES

For tubing outside a furnace zone, use the temperature of the oil or vapor carried by the line.

This table divided by 6 gives the allowable working stresses which are plotted in Figure 4 (carbon steel) and Figure 5 for 4-6 percent chrome. It is well known that values presented here differ when reported by various metallurgical laboratories. These tables and graphs have worked out very well in practice.

With reference to creep; as stated previously in this paper, for heater tubes we know creep will proceed but it is slow and taken care of by careful inspection and

THE TEXAS COMPANY

GENERAL NOTES FORMULA AND ESTABLISHED MINIMUM WALL THICKNESSES FOR 0.15-0.20% CARBON & 4-6% CHROME - 0.16-0.25% CARBON SEAMLESS STEEL TUBING HEATER TUBES & OPERATING LINES

FORMULA USED

$$P = \frac{10\,[D_1^2 - D_2^2]}{13\,D_1^2 + 4\,D_2^2} \times S$$

P = Allowable Operating Pressure in #/□"
D_1 = Outside Diameter in Inches
D_2 = Inside " "
S = Allowable Unit Stress in #/□"

NOTES

1 – Temperatures and corresponding Allowable Unit Stresses shown in Table are for Metal Temperatures.

2 – Heater Tubes
"In Furnace" – This section shall include the entire length of the tube except five (5) inches at each end of the tube.
"In Box" – Five (5) inches from each end of the tube shall be considered as in Box.
(a) The minimum wall thickness for each of the two (2) sections of a Heater Tube shall be determined on the basis of the Operating Temperature and Pressure carried on same.
(b) Regardless of which section of the tube reaches the minimum thickness first, the tube shall be removed from service.

3 – The Radiant Sections of Heaters shall be considered as follows :–
"H.M.V.S." – Side-Wall and Lower three (3) rows of tubes.
"Kellogg" – Side-Wall, Roof and two (2) top rows back of bridge wall.
"De Florez" – Vertical tubes and Bottom three (3) rows of economizer tubes.

4 – Metal Temperatures
(a) Heater Tubes
"In Furnace" – The metal temperature of this section of the tube shall be taken as follows :–
150° F. above the oil for tubes in the Radiant Section of Dirty Circulating Heaters.
100° F. above the oil for tubes in the Radiant Section of Reforming and Clean Circulating Heaters.
100° F. above the oil for tubes in the Convection Sections of all Heaters.
"In Box" – The metal temperature of this section of the tube shall be taken as being the same temperature as the oil passing through the tube.
(b) Operating Lines :–
The metal temperature of lines shall be taken as being the same temperature as the oil or vapors passing through the line.

5 – Following Tabulation gives the Absolute Minimum Thicknesses that either Plain Carbon or Low Chrome Heater Tubes and Operating Lines shall be allowed to reach in service on the different types of Units, regardless of the Operating Temperature or Pressure carried on same.

6 – The minimum wall thickness required for Heater Tubes or Operating Lines on each individual Cracking Unit shall be determined, based on the actual temperature and pressure conditions on the tubing in question, and if a greater wall thickness is required than the absolute minimum shown in table, tubes and lines shall be removed from service when the required minimum thickness is reached.

MINIMUM ALLOWABLE THICKNESSES

PRESSURE UNITS

O. D. OF TUBING	HEATER TUBES		OPERATING LINES			
			UNITS OPERATING ABOVE 200#/□" SUCH AS H.M.V.S., CROSS, ETC.		UNITS OPERATING BELOW 200#/□" SUCH AS P.C.S., D.C.U., T.S., ETC.	
	MIN. WALL THICKNESS		MIN. WALL THICKNESS		MIN. WALL THICKNESS	
	IN FURNACE	IN BOX	AT TEMP. ABOVE 650° F	AT TEMP. BELOW 650° F	AT TEMP. ABOVE 650° F	AT TEMP. BELOW 650° F
			CONDITIONS FOR SELECTION			
			700#/□" @ 950°	800#/□" @ 650°	500#/□" @ 1000°	600#/□" @ 650°
1 5/8"			0.10"	0.10"	0.10"	0.10"
1 1/2"			0.10"	0.10"	0.10"	0.10"
1 3/8"			0.10"	0.10"	0.10"	0.10"
2 3/8"			0.12"	0.10"	0.11"	0.10"
2 1/2"			0.15"	0.10"	0.12"	0.10"
3 1/4"	0.16"	0.12"	0.16"	0.12"	0.13"	0.12"
3 1/2"	0.18"	0.15"	0.18"	0.12"	0.15"	0.12"
4"	0.20"	0.16"	0.20"	0.14"	0.17"	0.12"
4 1/2"	0.22"	0.17"	0.22"	0.15"	0.20"	0.12"
5"	0.27"	0.21"	0.27"	0.17"	0.22"	0.13"
5 5/8"			0.29"	0.19"	0.24"	0.15"
6 5/8"			0.34"	0.23"	0.28"	0.17"
8 5/8"			0.44"	0.30"	0.37"	0.22"
13 1/2"			0.75"	0.46"	0.57"	0.34"

CRUDE TOPPING & PIPE STILL UNITS

O. D. OF TUBING	HEATER TUBES		OPERATING LINES
			UNITS OPERATING AT 25#/□" OR LESS ON FRACTIONATING TOWERS
	MIN. WALL THICKNESS		MIN. WALL THICKNESS
	IN FURNACE	IN BOX	AT TEMPERATURES OF 700° F. & BELOW
			CONDITION FOR SELECTION
			200#/□" @ 700° F.
1 5/8"			0.09"
1 1/8"			0.09"
1 1/8"			0.09"
2 3/8"			0.09"
2 1/2"	0.12"	0.10"	0.09"
2 3/4"	0.12"	0.10"	0.09"
3 1/4"	0.12"	0.10"	0.10"
3 3/4"	0.12"	0.10"	0.10"
3 1/2"	0.12"	0.10"	0.10"
4"	0.12"	0.10"	0.11"
4 1/2"	0.14"	0.12"	0.12"
4 3/4"	0.15"	0.13"	0.13"
5"	0.16"	0.14"	0.14"
5 5/8"			0.15"
6 5/8"			0.15"
8 5/8"			0.15"

REFERENCE DWGS.

Dwg 14-882 - Allowable Working Stress Curve for 0.15-0.20% Carbon Seamless Steel Tubing
Dwg. 14-883 - Allowable Working Stress Curve for 4-6% Chrome - 0.15-0.25% Carbon Seamless Steel Tubing.
Dwg 14-925 - Table A.O.P. 0.15-0.20% Carbon Seamless Steel Tubing.
Dwg. 14-926 - Table A.O.P. 4-6% Chrome - 0.16-0.25% Carbon Seamless Steel Tubing.

CALCULATED BY H.G.H.
CHECKED BY F.T.S.

APPROVED BY	DATE
Ref	9-30-33

DATE 8-30-33

DWG. №14-924

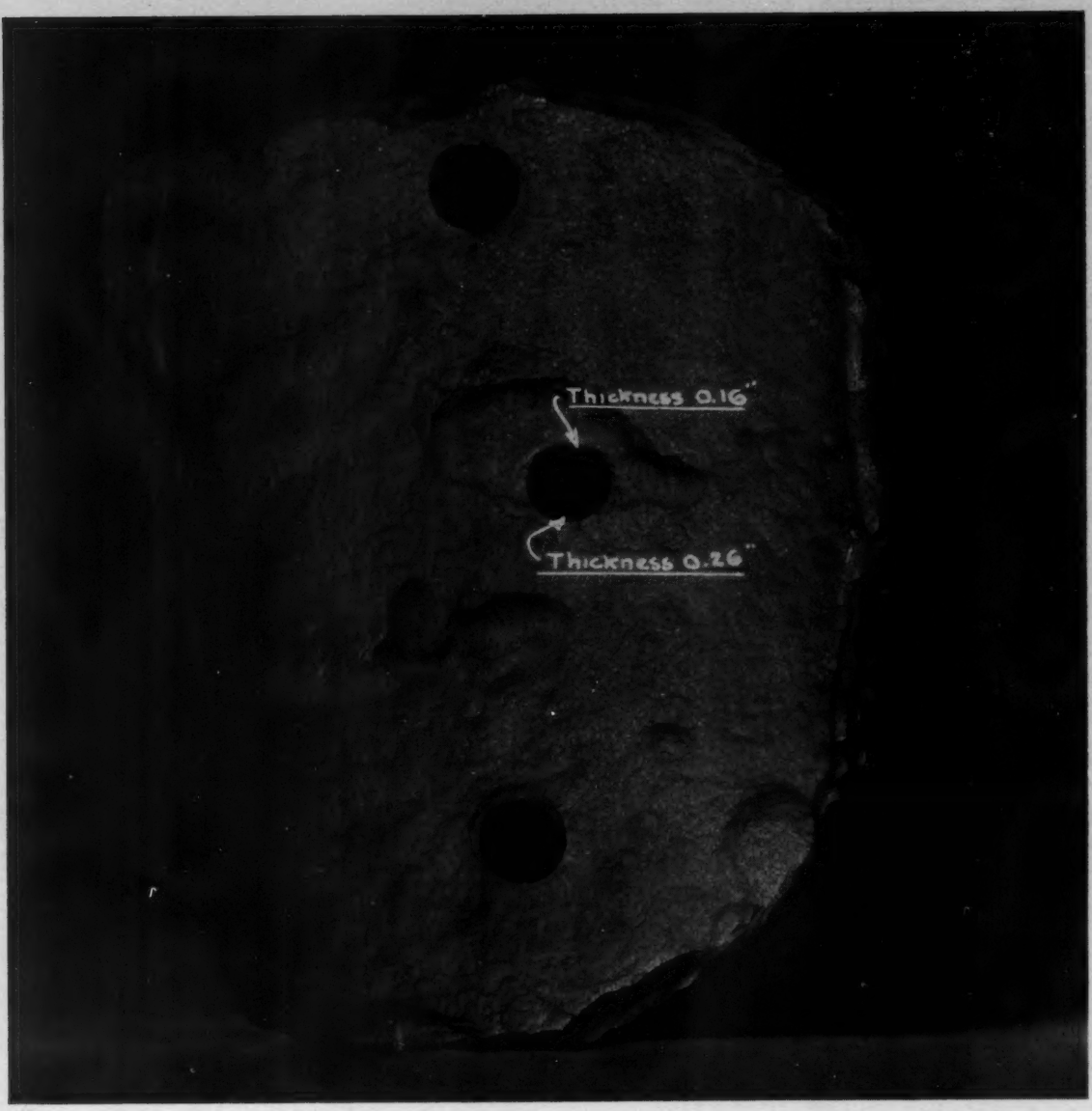


PHOTO 19017

removal from service. With outside lines, inspection should detect creep and lines will be removed.

A chart has been published by the National Tube Company showing long time creep of various steels (1 percent in 10,000 hours). The curve for carbon steel has been copied and Figure 6 shows that it does not differ greatly from our Drawing 14-882 which was compiled by dividing the ultimate strength by 6.

The use of this system contemplates the compilation of tables.

Drawing No. 14-925 is a portion of these tables for carbon steel; No. 14-926 for 4-6 percent chrome.

These are introduced not to give or recommend The Texas Company values but to show the type of information recommended for every operating unit.

The minimum practical thickness allowed in a tube is important. Even if a metal for a tube should be developed giving very high creep strength, no one would consider operating a knife-blade wall thickness. Corrosion is characterized by some pitting; the inspector may not locate the thinnest point in the line; there may be some slight error in tube measurement. In practice, lines are often condemned at quite an appreciable thickness above the theoretical thickness for rejection. Photo 19017 illustrates the need of a relatively thick tube at rejection, from practical considerations.

One side of the drilled hole is .26-inch the other side .16-inch. In this view there are several pits shown; also observe two previously drilled locations. Drawing No. 14-924 gives information with respect to minimum thicknesses.

Let the writer emphasize that no unit can safely operate and be inspected without some systematic procedure as outlined. It may not be this particular procedure; nor must the values used check with the ones here presented. But the system is important. Later it can be modified, if improperly chosen on the basis of positive records so as to be in proper accord with safety and economy.

Tubes for heaters, outside lines and vessels for pressure batteries must be selected and operated under a carefully compiled code of operation and inspection as outlined above. There are many other parts of pressure batteries where metallurgy plays an important part, some will be briefly commented upon.

With respect to pumps; an interesting article was published in *Metals Technology*—August, 1935, titled "TP-631—Materials Used in Oil Refinery Pumps," by A. E. Harnsberger. Supplementing this article we are

THE TEXAS COMPANY

TABLE OF ALLOWABLE OPERATING PRESSURES
0.15–0.20% CARBON SEAMLESS STEEL TUBING
HEATER TUBES & OPERATING LINES

SIZE OF TUBING IN INCHES	THICKNESS OF METAL IN INCHES	ALLOWABLE OPERATING PRESSURE IN #/□"												
		0-650°F S-10000#	700°F S-9665#	750°F S-9080#	800°F S-8330#	850°F S-7500#	900°F S-6670#	950°F S-5830#	1000°F S-5000#	1050°F S-4210#	1100°F S-3540#	1150°F S-2900#	1200°F S-2370#	1250°F S-1960#	1300°F S-1670#
5" x 3½"	0.75	3410	3295	3095	2840	2555	2275	1985	1705	1435	1205	990	810	670	570
	0.72	3280	3170	2980	2735	2460	2190	1915	1640	1380	1160	950	780	645	550
5" x 3⅜"	0.69	3140	3035	2850	2615	2355	2095	1830	1570	1320	1110	910	745	615	525
	0.66	3020	2920	2745	2515	2265	2015	1760	1510	1270	1070	875	715	590	505
5" x 3¾"	0.63	2870	2775	2605	2390	2150	1915	1670	1435	1210	1015	830	680	560	480
	0.60	2760	2665	2505	2300	2070	1840	1610	1380	1160	975	800	655	540	460
	0.57	2625	2540	2385	2185	1970	1750	1530	1315	1105	930	760	620	515	440
	0.54	2495	2410	2265	2075	1870	1665	1455	1245	1050	885	725	590	490	415
5" x 4"	0.50	2315	2235	2100	1930	1735	1545	1350	1155	975	820	670	550	455	385
	0.47	2180	2105	1980	1815	1635	1455	1270	1090	915	770	630	515	425	365
	0.44	2045	1975	1855	1700	1530	1365	1190	1020	860	725	590	485	400	340
	0.41	1905	1840	1730	1590	1430	1270	1110	955	800	675	555	450	375	320
5" x 4¼"	0.38	1745	1690	1585	1455	1310	1165	1020	875	735	620	505	415	340	290
	0.35	1630	1575	1480	1360	1225	1090	950	815	685	580	475	385	320	275
	0.32	1495	1445	1355	1245	1120	995	870	745	630	530	435	355	295	250
	0.29	1355	1310	1230	1130	1015	905	790	680	570	480	395	320	265	225
	0.27	1265	1220	1145	1050	945	840	735	630	530	445	365	300	250	210
5" x 4½"	0.25	1170	1130	1060	975	880	780	680	585	495	415	340	275	230	195
	0.23	1075	1040	980	895	810	720	630	540	455	380	310	255	210	180
	0.21	985	950	895	820	740	655	575	490	415	350	285	235	195	165
	0.18	845	815	765	705	635	565	490	420	355	300	245	200	165	140
	0.15	705	680	640	585	530	470	410	350	295	250	205	165	140	115
	0.12	565	545	510	470	425	375	330	280	235	200	165	135	110	95
	0.09	415	410	385	350	315	280	245	210	180	150	125	100	85	70
5⅜" x 4⅛"	0.44	1830	1770	1660	1525	1375	1220	1065	915	770	650	530	435	360	305
	0.40	1675	1620	1520	1395	1255	1120	975	840	705	595	485	395	330	280
	0.37	1550	1500	1410	1295	1165	1035	905	775	655	550	450	370	305	260
	0.34	1425	1380	1295	1190	1070	950	830	715	600	505	415	340	280	240
	0.31	1305	1260	1185	1085	975	870	760	650	550	460	380	310	255	220
	0.28	1180	1140	1070	980	885	785	685	590	495	415	340	280	230	195
	0.25	1055	1020	955	875	790	700	615	525	445	375	305	250	205	175
	0.23	970	935	880	805	725	645	565	485	410	345	280	230	190	160
	0.20	845	815	765	700	630	560	490	420	355	300	245	200	165	140
	0.18	760	735	690	630	570	505	440	380	320	270	220	180	150	125
	0.15	635	610	575	525	475	420	370	315	265	225	185	150	125	105
	0.12	505	490	460	420	380	340	295	255	215	180	145	120	100	85
6⅝" x 5⅜"	0.62	2185	2115	1985	1820	1640	1460	1275	1095	920	775	635	520	430	365
	0.59	2065	1995	1875	1720	1550	1380	1205	1035	870	730	600	490	405	345
	0.56	1965	1900	1785	1635	1475	1310	1145	980	825	695	570	465	385	330
	0.53	1860	1800	1690	1550	1395	1240	1085	930	785	660	540	440	365	310
	0.50	1755	1700	1595	1465	1320	1170	1025	880	740	620	510	415	345	295
	0.47	1655	1600	1500	1380	1240	1105	965	825	695	585	480	390	325	275
	0.44	1550	1500	1405	1290	1165	1035	905	775	655	550	450	365	305	260
	0.41	1445	1395	1310	1205	1085	965	840	725	610	510	420	340	285	240
	0.37	1305	1260	1185	1090	980	870	760	655	550	460	380	310	255	220
	0.34	1200	1160	1090	1000	900	800	700	600	505	425	350	285	235	200
	0.31	1095	1060	995	910	820	730	640	550	460	390	320	260	215	185
	0.28	990	955	900	825	745	660	575	495	415	350	285	235	195	165
	0.25	885	855	805	735	665	590	515	445	375	315	255	210	175	150
	0.22	780	755	705	650	585	520	455	390	330	275	225	185	155	130
	0.18	640	615	580	530	480	425	370	320	270	225	185	150	125	105
	0.15	530	515	485	445	400	355	310	265	225	190	155	125	105	90
	0.12	425	410	385	355	320	285	250	215	180	150	125	100	85	70
6⅞" x 7⅛"	0.75	2020	1950	1835	1680	1515	1345	1175	1010	850	715	585	480	395	335
	0.72	1940	1875	1760	1615	1455	1295	1130	970	815	685	565	460	380	325
	0.69	1860	1800	1690	1550	1395	1240	1085	930	785	660	540	440	365	310
	0.66	1780	1720	1615	1485	1335	1190	1040	890	750	630	515	420	350	295
8⅝" x 7⅛"	0.63	1690	1630	1535	1405	1265	1125	985	845	710	600	490	400	330	280
	0.60	1620	1570	1475	1350	1215	1080	945	810	685	575	470	385	320	270
	0.57	1540	1490	1400	1285	1155	1030	900	770	650	545	445	365	305	260
	0.54	1460	1415	1325	1220	1095	975	850	730	615	520	425	345	285	245
	0.50	1355	1310	1230	1130	1015	905	790	675	570	480	395	320	265	225
	0.47	1275	1230	1155	1060	955	850	745	635	535	450	370	300	250	215
	0.44	1195	1155	1085	995	895	800	695	600	505	425	345	285	235	200
	0.41	1110	1075	1010	925	835	740	650	555	470	395	320	265	220	185
	0.38	1030	995	935	860	775	690	600	515	435	365	300	245	200	170
	0.35	950	920	865	790	715	635	555	475	400	335	275	225	185	160
	0.32	870	840	790	725	650	580	505	435	365	310	250	205	170	140
	0.29	790	760	715	655	590	525	460	395	330	280	230	185	155	130
	0.25	680	660	620	565	510	455	395	340	285	240	195	160	135	115
	0.22	600	580	545	500	450	400	350	300	250	210	175	140	115	100
	0.18	490	475	445	410	370	325	285	245	205	175	140	115	95	80
	0.15	410	395	370	340	305	275	240	205	170	145	120	95	80	70

REFERENCE DRAWINGS

DWG. 14-882 – Allowable Working Stress Curve for 0.15-0.20% Carbon Seamless Steel Tubing.
DWG. 14-924 – General Notes, Formula & Established Minimum Wall Thicknesses for 0.15-0.20% Carbon and 4-6% Chrome – 0.16-0.25% Carbon Seamless Steel Tubing.

CALCULATED BY M.A.H.
CHECKED BY R.T.S.

APPROVED BY	DATE
R.T.S.	9-30-33

DATE 8-30-33 SHEET No. 3 OF 4 SHEETS

DWG. No. 14-925

THE TEXAS COMPANY

TABLE OF ALLOWABLE OPERATING PRESSURES
4-6% CHROME — 0.16-0.25% CARBON — SEAMLESS STEEL TUBING
HEATER TUBES & OPERATING LINES

SIZE OF TUBING IN INCHES	THICKNESS OF METAL IN INCHES	ALLOWABLE OPERATING PRESSURE IN #/□"																
		0-500°F 10000%	550°F 9920%	600°F 9750%	650°F 9460%	700°F 9050%	750°F 8620%	800°F 8070%	850°F 7500%	900°F 6950%	950°F 6400%	1000°F 5840%	1050°F 5290%	1100°F 4720%	1150°F 4170%	1200°F 3620%	1250°F 3050%	1300°F 2500%
5" x 3¼"	0.75	3410	3380	3325	3225	3085	2940	2750	2555	2370	2180	1990	1805	1610	1420	1235	040	850
	0.72	3280	3255	3200	3105	2970	2830	2650	2460	2280	2100	1915	1735	1550	1370	1190	1000	820
5" x 3½"	0.69	3140	3115	3065	2970	2845	2710	2535	2355	2185	2010	1835	1660	1485	1310	1135	960	785
	0.66	3020	3000	2945	2860	2735	2605	2440	2265	2100	1935	1765	1600	1425	1260	1095	920	755
5" x 3¾"	0.63	2870	2845	2795	2715	2595	2475	2315	2150	1995	1835	1675	1520	1355	1195	1040	875	715
	0.60	2760	2735	2690	2610	2495	2380	2225	2070	1920	1765	1610	1460	1300	1150	1000	840	690
	0.57	2625	2605	2560	2485	2375	2265	2120	1970	1825	1680	1535	1390	1240	1095	950	800	655
	0.54	2495	2475	2430	2360	2255	2150	2010	1870	1735	1595	1455	1320	1175	1040	900	760	625
5" x 4"	0.50	2315	2295	2255	2190	2095	1995	1865	1735	1610	1480	1350	1225	1090	965	840	705	580
	0.47	2180	2160	2125	2060	1970	1875	1760	1635	1515	1395	1270	1150	1030	910	790	665	545
	0.44	2045	2025	1990	1935	1850	1760	1650	1530	1420	1310	1195	1080	985	850	740	625	510
	0.41	1905	1890	1860	1805	1725	1645	1540	1430	1325	1220	1115	1010	900	795	690	580	475
5" x 4¼"	0.38	1745	1730	1700	1650	1580	1505	1410	1310	1215	1115	1020	925	825	730	630	535	435
	0.35	1630	1615	1590	1545	1475	1405	1315	1225	1135	1045	955	865	770	680	590	500	410
	0.32	1495	1480	1455	1415	1350	1290	1205	1120	1040	955	870	790	705	625	540	455	375
	0.29	1355	1345	1320	1280	1225	1170	1095	1015	940	865	790	715	640	565	490	415	340
	0.27	1265	1255	1230	1195	1145	1090	1020	945	880	810	740	670	595	525	455	385	315
5" x 4½"	0.25	1170	1160	1140	1105	1060	1010	945	880	815	750	685	620	550	490	425	355	295
	0.23	1075	1070	1050	1020	975	930	870	810	750	690	630	570	510	450	390	330	270
	0.21	985	975	960	930	890	850	795	740	685	630	575	520	465	410	355	300	245
	0.18	845	835	825	800	765	730	680	635	585	540	495	445	400	350	305	255	210
	0.15	705	700	685	665	635	605	570	530	490	450	410	370	330	295	255	215	175
	0.12	565	560	550	535	510	485	455	425	390	360	330	300	265	235	205	170	140
	0.09	415	410	405	390	375	355	335	315	285	265	240	220	195	170	150	125	105
5⅝" x 4½"	0.44	1830	1815	1785	1730	1655	1575	1475	1375	1270	1170	1070	970	865	765	665	560	460
	0.40	1675	1665	1635	1585	1515	1445	1355	1255	1165	1075	980	885	790	700	605	510	420
	0.37	1550	1540	1515	1470	1405	1340	1250	1165	1080	995	905	820	735	645	560	475	390
	0.34	1425	1415	1390	1350	1290	1230	1150	1070	990	915	835	755	675	595	515	435	355
	0.31	1305	1295	1270	1235	1180	1125	1050	975	905	835	760	690	615	545	470	395	325
	0.28	1180	1170	1150	1115	1065	1015	950	885	820	755	690	625	555	490	425	360	295
	0.25	1055	1045	1025	995	955	910	850	790	730	675	615	555	495	440	380	320	265
	0.23	970	960	945	915	875	835	780	725	675	620	565	515	455	405	350	295	240
	0.20	845	835	820	795	765	725	680	630	585	540	490	445	400	350	305	255	210
	0.18	760	755	740	720	685	655	615	570	530	485	445	405	360	315	275	230	190
	0.15	635	630	615	600	575	545	510	475	440	405	370	335	300	265	230	195	160
	0.12	505	505	495	480	460	435	410	380	350	325	295	270	240	210	185	155	125
6⅝" x 5⅜"	0.62	2185	2170	2130	2070	1980	1885	1765	1640	1520	1400	1275	1155	1030	910	790	665	545
	0.59	2065	2050	2015	1955	1870	1780	1665	1550	1435	1320	1205	1095	975	860	750	630	515
	0.56	1965	1950	1915	1860	1775	1695	1585	1475	1365	1255	1145	1040	925	820	710	600	490
	0.53	1860	1845	1815	1760	1685	1605	1500	1395	1295	1190	1085	985	880	775	675	570	465
	0.50	1755	1745	1715	1660	1590	1515	1420	1320	1220	1125	1025	930	830	735	635	535	440
	0.47	1655	1640	1615	1565	1495	1425	1335	1240	1150	1060	965	875	780	690	600	505	415
	0.44	1550	1540	1510	1465	1405	1335	1250	1165	1075	990	905	820	730	645	560	475	390
	0.41	1445	1435	1410	1365	1310	1245	1165	1085	1005	925	845	765	680	605	525	440	360
	0.37	1305	1295	1275	1235	1180	1125	1055	980	910	835	765	690	615	545	475	400	325
	0.34	1200	1190	1170	1135	1085	1035	970	900	835	770	700	635	565	500	435	365	300
	0.31	1095	1085	1070	1035	990	945	885	820	760	700	640	580	515	455	395	335	275
	0.28	990	980	965	935	895	855	800	745	690	635	580	525	465	415	360	300	250
	0.25	885	880	865	835	800	765	715	665	615	565	515	470	420	370	320	270	220
	0.22	780	775	760	735	705	670	630	585	540	500	455	415	370	325	280	240	195
	0.18	640	635	620	605	575	550	515	480	445	410	375	340	300	265	230	195	160
	0.15	530	530	520	505	480	460	430	400	370	340	310	280	250	220	195	160	135
	0.12	425	425	415	405	385	365	345	320	295	275	250	225	200	180	155	130	105
6⅝" x 7⅛"	0.75	2020	2005	1970	1910	1825	1740	1630	1515	1405	1290	1180	1070	955	840	730	615	505
	0.72	1940	1925	1890	1835	1755	1670	1565	1455	1350	1240	1135	1025	915	810	700	590	485
	0.69	1860	1845	1815	1760	1685	1605	1500	1395	1295	1190	1085	985	880	775	675	570	465
	0.66	1780	1765	1735	1685	1610	1535	1435	1335	1240	1140	1040	940	840	745	645	545	445
6⅝" x 7⅜"	0.63	1690	1675	1645	1595	1530	1455	1360	1265	1175	1080	985	895	795	700	610	515	420
	0.60	1620	1610	1580	1535	1470	1400	1310	1215	1125	1040	945	860	765	675	585	495	405
	0.57	1540	1530	1505	1460	1395	1330	1245	1155	1070	990	900	815	730	645	560	470	385
	0.54	1460	1450	1425	1385	1325	1260	1180	1095	1015	935	855	775	690	610	530	445	365
	0.50	1355	1345	1320	1280	1225	1165	1095	1015	940	865	790	715	640	565	490	415	340
	0.47	1275	1265	1240	1205	1155	1100	1030	955	885	815	745	675	600	530	460	390	320
	0.44	1195	1185	1165	1130	1080	1030	965	895	830	765	700	635	565	500	435	365	300
	0.41	1110	1105	1085	1050	1005	960	895	835	775	710	650	590	525	465	405	340	280
	0.38	1030	1025	1005	975	935	890	835	775	715	660	605	545	485	430	375	315	260
	0.35	950	940	925	900	860	820	765	715	660	610	555	505	450	395	345	290	240
	0.32	870	860	845	820	785	750	700	650	605	555	505	460	410	360	315	265	215
	0.29	790	780	770	745	715	680	635	590	550	505	460	415	370	330	285	240	195
	0.25	680	675	665	645	615	585	550	510	475	435	400	360	320	285	245	210	170
	0.22	600	595	585	565	540	515	485	450	415	385	350	315	285	250	215	185	150
	0.18	490	485	480	465	445	420	395	370	340	315	285	260	230	205	175	150	125
	0.15	410	405	400	385	370	350	330	305	285	260	240	215	195	170	145	125	100

CALCULATED BY B.G.H.
CHECKED BY F.T.S.

REFERENCE DRAWINGS

DWG. 14-883 - Allowable Working Stress Curve for 4-6% Chrome — 0.16-0.25% Carbon Seamless Steel Tubing.
DWG. 14-924 - General Notes, Formula & Established Minimum Wall Thicknesses for 0.15-0.20% Carbon and 4-6% Chrome - 0.16-0.25% Carbon Seamless Steel Tubing.

APPROVED BY	DATE
R.L.P.	9-30-33

DATE: 8-30-33

SHEET Nº 3 OF 3 SHEETS

DWG. Nº14-926

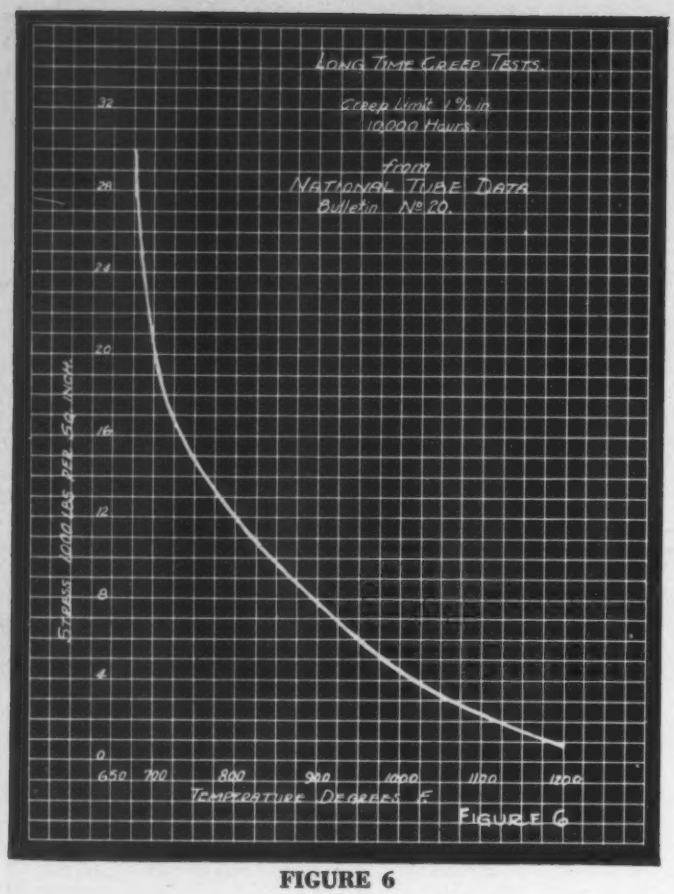


FIGURE 6

presenting several items representing The Texas Company practice.

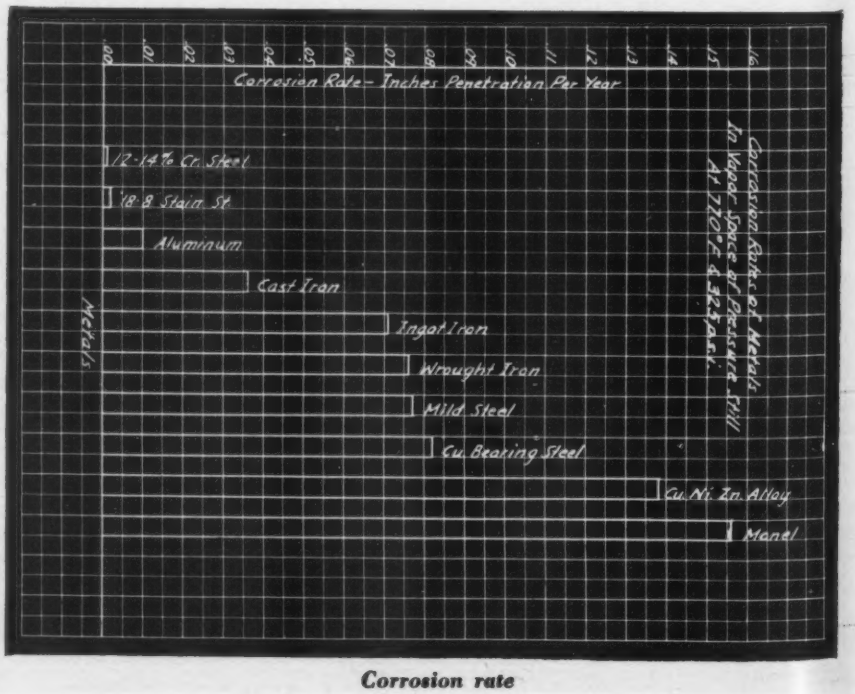
For pump rods we find that a die steel containing 1.5 to 2 percent carbon, 12-14 percent chromium with small percentages of vanadium and molybdenum gives excellent service. This should be heat treated to a Brinell Number of 500. It resists corrosion and abrasion, and although high in first cost the life of these rods runs as high as three years depending on the care used with packing the pump; also the rejected rod has a re-usable value—it can be used for smaller rods. In many refineries 18-8 has given excellent service but is not as resistant to abrasion.

Liners for pumps: The high chromium alloys have been used but because of their cost, 4-6 percent chrome-molybdenum liners are now being substituted. They are not so resistant to corrosion; however, the relatively low price and ability to purchase them locally are an advantage. It is customary to line the ports of pressure pumps with 18-8 and to use stainless steel of 12-14 percent chrome analysis for valves and pistons. One problem which has never been solved is the selection of proper rings for pumps. Cast iron is standard and although many special cast iron analyses have been used it is customary to renew rings after each run of the battery. When substituting other alloys it is found that although they resist corrosion, mechanically they do not make good rings.

The refiner should consider 5 percent chrome for pressure castings, such as return bends and pressure valves where corrosion is severe. These frequently have machine work and the increased cost of the finished article is not greatly in excess of chrome-nickel steels which have been standard heretofore. For guidance with respect to the price of 5 percent chrome castings; $0.15 to $0.17 per pound has been quoted depending on the foundry. Actual service record from these castings when used for U-bends indicates a life at least four times as long as carbon steel and there is absence of the pitting so general with carbon steel.

An item of interest is the excellent service which has been obtained from 18-8 when pressed into bubble caps. These caps cost approximately three times that of cast iron which are so generally used; their advantages are lightness in weight, practically no corrosion, and absence of breakage. Disadvantages are the extra price compared to cast iron and the fact that with so many different sizes and shapes of caps the expenditure for dies is considerable. Should a refiner standardize on one shape and one size cap then the pressed 18-8 cap would have merit. The Texas Company has installed pressed trays of 18-8 and their service has been excellent. The high cost forbids extensive consideration but they were light in weight and practically non-corrosive. Caps and trays have been in service for approximately seven years.

The modern cracking coil is composed of long tubes suspended at each end in a hot furnace. To prevent sagging of these tubes, supports are necessary. It has been customary to use steel supports protected by refractory material. These have not been satisfactory because of the high maintenance, and the fact that the bulky refractory material obstructs the view of the tube from the operator. Alloys of high chromium and nickel of various percentages have been used successfully, they do not scale and have high strength. It is not the purpose of this paper to classify these various alloys. One disadvantage with them has been the tendency to become brittle at the end of various runs of the battery when the metal is cold. It is understood that manufacturers of these castings are able to produce heat resisting castings where this brittleness is not experienced. Requisitions for these castings should contain some



Corrosion rate

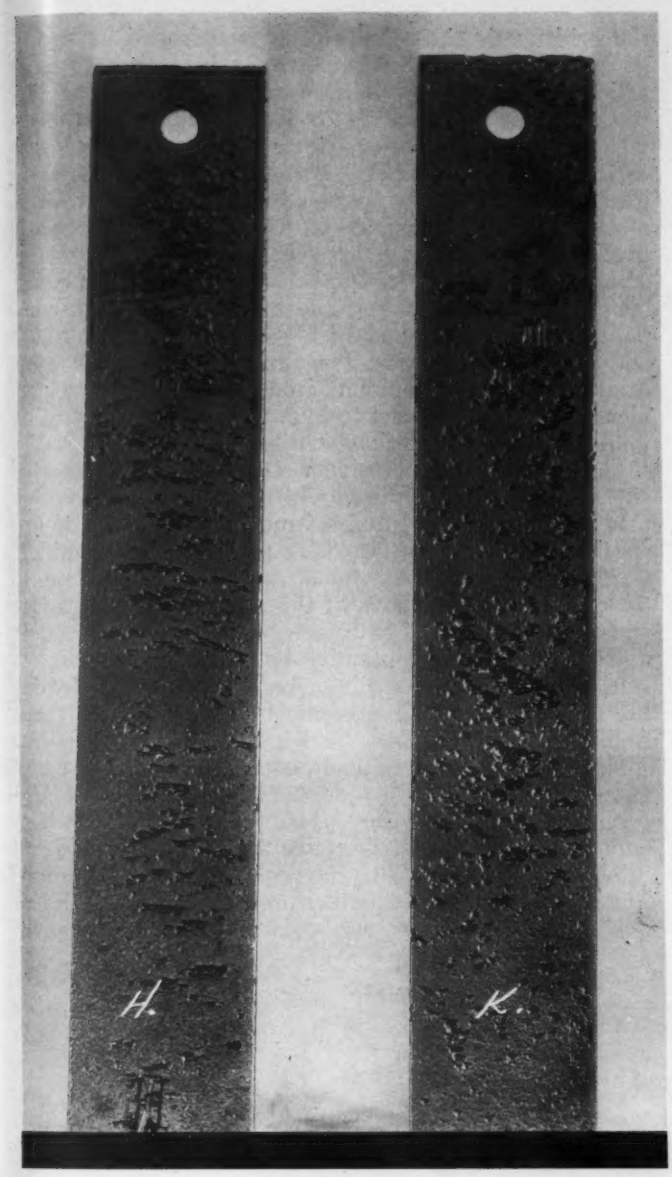


PHOTO 10556

We have on record the use of aluminum for roofs of tanks, this being satisfactory but costly. Galvanized iron has been used for corrosive tanks; here again the question of how long the normal roof would last and how much added life galvanizing will give, is important. This item appears to have considerable merit.

Little that is new can be offered with respect to the choice of metals for various equipment around the plants, such as tanks, running lines, etc.

PREVENTION OF CORROSION—PROTECTIVE COATINGS

No paper on corrosion prevention is complete without mention of protective coatings.

We are all more or less familiar with the general types of paints used to protect steel from atmospheric corrosion. However, there are many abnormal corrosive conditions around a refinery in which ordinary paints do not give satisfactory protection. For steel exposed to water spray; as for example tank roofs which are sprayed to reduce evaporation losses, or structures in the vicinity of cooling towers we have found thick fibrous asphaltic materials to give better protection than paint coatings. These coatings may be brushed, sprayed or troweled on, the more plastic compounds give the best protection.

For resistance to acids and alkalis we find paints formulated on a chlorinated rubber base and also from crepe rubber hydrocarbons show decided advantages over the orthodox type paints. The former type, because of their insolubility in petroleum hydrocarbons show some promise as protective coatings for use in the vapor space of tanks.

It is not the purpose of this paper to discuss inspection of equipment but mention must be made that The Texas Company has an extensive system of inspection and keeping of records so that the exact condition of each line and each part of their equipment is well known. The metallurgist has had an active part in this system.

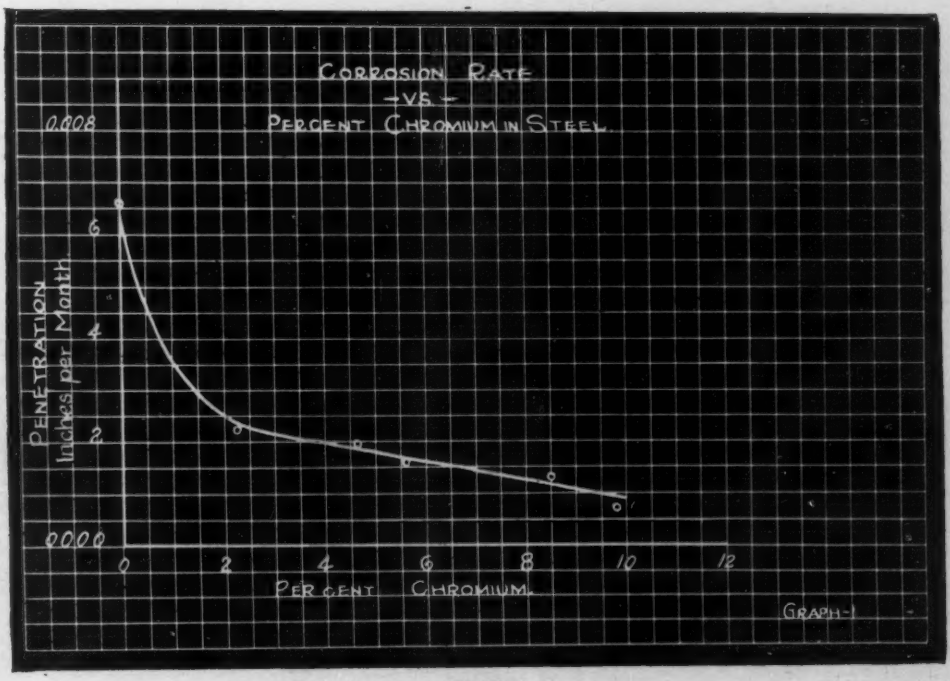
STUDY OF CORROSION

Several years ago, refiners experienced rapid corrosion of their equipment because of corrosive crudes. Not only were replacements necessary but also knowl-

clause to the effect that they must not be brittle when cold.

The metallurgist has not been as active in selection of metals for non-pressure refining equipment as he has for pressure equipment; service is less severe, and the corrosion rates are not so high. A few items of importance are listed.

For tube stills; the greatest problem is that of tubes for shell and tube exchangers; this has been covered in a separate portion of this paper. Ammonia is used for neutralization, this being a problem for the oil chemist and operator. The usual careful inspection, keeping of records and replacement of equipment is in vogue with this equipment rather than the use of expensive alloys.



GRAPH 6

edge of the safety of furnace tubes, pressure lines, pressure vessels, valves and other equipment was very vague. Fires were frequent and costly and it was evident that some method must be found to evaluate the rate of corrosion of carbon steel in equipment and also select new alloys more resistant to corrosion than ordinary steel. Accordingly, specimens of various alloys were hung in different locations in various units, the loss in weight of each metal being a measure of its resistance to corrosion. This procedure has been standard for at least 15 years. Hundreds of specimens have been installed in vessels, lines, exchangers and other parts of most units. Advance information is obtained with reference to the rate of corrosion of the metal already installed as the structure of a unit as well as indications as to more suitable alloys which should be substituted. These specimens of metals, after preliminary cleaning and weighing, are placed in certain locations where the rate of corrosion is desired. After a definite time, they are removed, cleaned, weighed and the loss of weight computed in terms of inches of penetration per 1000 hours or inches of penetration per year. This method of test is not exact to the extent that with a series of five test specimens of the same metal, we expect each specimen to give the same corrosion value (inches of penetration). That is, duplicate specimens often will not check within 10 percent. On the other hand, a series of specimens of one metal will show in all cases a different corrosion rate from a series of specimens from a radically different metal. For example, a series of five specimens of copper exposed to hydrogen sulphide corrosion for a suitable time may not check closely one with the other but when compared with a series of five specimens of 18-8, the evidence is clear that copper is corroded by hydrogen sulphide and 18-8 is remarkably resistant to its action. The above is written to caution against expecting too much of this method of testing. Refer to the attached chart "Corrosion Rates of Metals in Vapor Space of Pressure Still." The metals ingot iron, wrought iron, mild steel and copper-bearing steel are all ferrous metals. The specimen method of test is not sufficiently precise to differentiate between the members of this series of metals. Now, compare these with 70 percent copper, 30 percent nickel, and monel; then again compare them with 18-8 and 12-14 percent chromium alloys and also with aluminum. Thus an appraisal of the value of stainless steel, aluminum, iron and steel, and copper-nickel alloy with respect to hydrogen sulphide corrosion under operating conditions can be made.

In like manner, corrosive water, acids or any corrosive agent can be appraised with respect to its corrosion rate on any selected group of metals. By means of test specimens the type of corrosive agent can be identified. Certain alloys such as monel, are highly resistant to mineral acid, other alloys of the stainless steel class are resistant to water and hydrogen sulphide. By suspending a group of samples containing both Monel and stainless steel in a corrosive medium, one can usually identify the type of corrosion present. If the Monel corrodes rapidly and the stainless steel is resistant to the corrosion, one infers that sulphide corrosion is taking place. If the stainless steel corrodes and monel resists, the inference is, acid corrosion. There are instances where both monel and stainless steel corrode and both acid and sulphide are present. This happened with certain pumps on treating units where neither bronze parts nor stainless steel parts are satisfactory and replacements frequent.

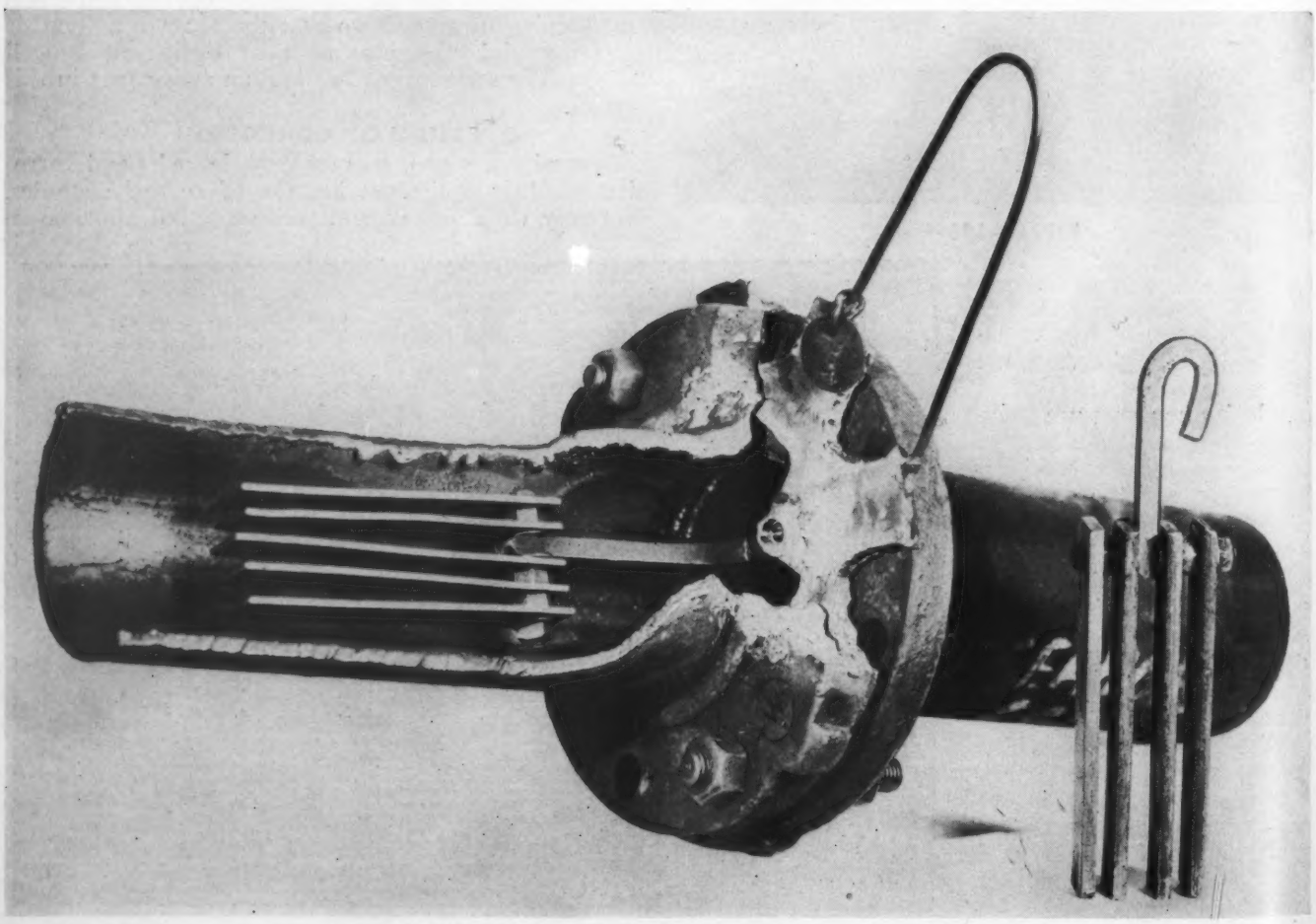


PHOTO 11732

Various refiners have, at one time or another, experimented with different sizes and shapes of test specimens. The specimen must not be too heavy or bulky. It must have a large area for a given weight. It is desirable to have the test bar large enough and of such a shape that physical tests may be made after corrosion testing. Some years ago, the Committee on Corrosion of the American Petroleum Institute adopted a test procedure including a standard bar. The following procedure is well in line with the A.P.I. code for corrosion testing. It is recommended for refiners who are concerned over their corrosion problems.

CORROSION TEST PROCEDURE

The specimen is 6 x 1 x ⅛-inch with a ¼-inch hole located ½-inch from one end. Photograph 10556 shows two specimens after exposure in a fuel oil sludge line.

These specimens are bolted together to comprise an assembly. Photograph 11732 shows an assembly installed in a line. The nuts, spacers, bolts and other parts of this assembly are stainless steel or other material exceptionally resistant to the presumed corrosive. In any assembly one of the various metals tested usually should be carbon steel which becomes the yardstick by which other alloys are appraised. Occasionally some other metal than carbon steel will be the reference metal.

The specimens tested should be properly cleaned of impurities or scale using emery if necessary; after exposure, specimens should be cleaned with a soft wire brush and gasoline and dried by a brief heating to about 300°F. before weighing. Care should be taken that all foreign material and corrosion products are removed without removing any metal.

The sample should be weighed in grams to the third decimal place. Corrosion results should be expressed as an average penetration in inches per 1000 hours on stream, or inches penetration per year. Data are the loss in weight, initial area exposed, hours exposed, specific gravity of the alloy.

Calculated corrosion is illustrated in the chart below:

METHOD OF CALCULATING CORROSION

$$\text{Penetration (Inches/Yr.)} = \frac{\text{Loss in Grams}}{\text{Hours on Test}} \times \frac{8760 \text{ (Hours per Yr.)}}{\text{Gms/cu. in. wgt} \times \text{Exposed Area in sq. in}}$$

$$\text{Constant Factor for Specimen} = \frac{8760}{\text{gms./cu. in.} \times \text{area}}$$

$$\text{Therefore, Penetration} = \text{Factor} \times \frac{\text{Loss, gms.}}{\text{Hours on Test}}$$

Standard Corrosion Specimen—⅛" to ⅜" thick x 1" wide x 6" long.

Areas of Specimens		Factors for Iron Base Alloys
⅛" x 1" x 6"	13.75 sq. in.	4.94
3/16" x 1" x 6"	14.62 sq. in.	4.67
¼" x 1" x 6"	15.50 sq. in.	4.41
⅜" x 1" x 6"	17.25 sq. in.	3.96

Photograph 15845 shows the method of installing test bars in a gasoline vapor line of a low pressure still. Use is made of a special steel gasket between the two flanges; samples are suspended as shown.

For several common metals the factors are as follows:

Metal	Thickness, Inch	Weight, Cu. Ft.	Weight, Gms./Cu. In.	Factor
Aluminum	¼	0.098	44.4	12.7
Brass (70:30)	¼	0.308	140	4
Cast Iron	¼	0.261	118	4.8
Copper	¼	0.321	145	3.9
Monel	¼	0.318	144	3.9
Stainless Steel	¼	0.283	128	4.4
Steel	¼	0.283	128	4.4

$$\text{Factor } \frac{8760}{\text{gms./cu. in.} \times \text{area}}$$

Having made a preliminary survey by means of specimens, the next step is to install several lines, heater tubes, exchanger tubes or whatever is under observation, made of alloys which showed well on the above tests. These are placed in actual service. If their performance checks with experimental data from corrosion specimens the problem is fairly well solved and full scale installations take place.

Some years ago, it was evident that stainless steels containing chromium (12 percent minimum) resisted sulphide corrosion remarkably well. The question arose as to how little chromium may be used and still obtain resistance to sulphide corrosion. A series of specimens of steel containing approximately 0-2, 4, 6, 8, 10 percent chromium were suspended in stills of cracking units, using the method of test explained above. The results of tests are shown in Graph 6, "Corrosion Rate vs. Percent Chromium in Steel." This was the procedure of developing the 4-6 percent chromium steels so widely used in cracking units for various parts. From this graph one will observe that 2 percent chromium should give reduced rates of corrosion relative to steel. 5 percent chromium should be an intermediate between the 2 percent chromium steel and the stainless steel range. Considerable 2 percent chromium steel is now being used.

The following information from sources outside The Texas Company gives a comparison of these steels.

Corrosion Rates of Various Steels in Different Locations of Cracking Unit—Rate of Carbon Steel—100

Carbon Steel	2 Percent Chrome Steel	4 Percent Chrome Steel
100	12	8
100	6	3
100	13	8

This information was obtained by use of corrosion test specimens described above. No information is available with reference to service life of 2 percent chrome steel. Its use is recent. Depending upon the corrosion rate of the crude charge we expect at least four times the service from 5 percent chrome as we do from carbon steel and this is borne out in practice. The more corrosive the crude the more valuable is 5 percent chrome steel. In cases where 5 percent chrome is not four times as good as carbon steel, and we have such instances, then carbon steel should be used.

The 4-6 percent chrome has a definite place in refinery service. It must not be used without careful preliminary study. Its best service is obtained at temperatures above 600°F. and in locations where steel fails from sulphide corrosion. It has been tried in cooler lines and in many cases it is not superior to carbon steel.

EXCHANGER TUBES

Modern refinery equipment makes use of many small tubes in shell and tube type exchangers. These tubes which are mainly ⅝, ¾ and 1-inch O.D. vary in length to meet the requirements of the refiners and conditions of operations. In the Port Arthur Works of The Texas Company there are approximately 165,000 tubes of the above sizes varying in length from 18 inches to 20 feet. The most common size is ¾-inch O.D. 16 Bwg. and the most common length is 12 feet, with 10-foot and 12-foot, 11-inch lengths running close seconds. Frequent and costly replacements have to be made. During the year 1936 approximately 56,000 such replace-

ments were made in The Texas Company's refinery in Port Arthur alone.

Originally the material used for these tubes was largely Admiralty metal and failure occurred after a service ranging from 6 months to 4 years, with 18 months as an average, depending on the temperature, materials handled, etc. Failure of these tubes was due mainly to dezincification. Where the temperature of the cooling water is high—180°F.—the failures are rapid and where this temperature is kept low—100°F.—the life of the tubes is much longer.

Much work has been done in selecting a better tube material. Large installations of 18-8 stainless steel have been made with disappointing results. The main failures were due to cracking and water pitting. In order to eliminate the water pitting which was first thought to be due to impurities in the metal and later believed to be due to particles of oxygen attaching themselves to the wall and starting electrolytic attack, we obtained 3700 tubes with a highly polished inside wall. These tubes were no better than the others. In view of the rapid failures and the fact that the price is out of line with respect to the price of Admiralty metal no further consideration has been given the 18-8 alloy for condenser tubes, nor have the manufacturers developed their tubes to where pitting and cracking have been eliminated.

Table 1 is a tabulation of various alloys tested with relative rates of corrosion in water cooled exchangers and relative prices as compared to Admiralty metal. In this table Admiralty metal is listed as having a life and price of 1, and the life and price of each of the other alloys are based on that of Admiralty. All were 16-gauge tubes.

As shown in this tabulation, red brass is far superior to Admiralty with respect to dezincification; however there are services where the Admiralty is superior to red brass. In oils containing a high percentage of sulphide the red brass which has a higher copper content fails more rapidly than the Admiralty.

The copper lined Admiralty tubes are superior to straight Admiralty, however, due to their increased cost they are not equal to red brass in all services. This bi-metal tube, however, has proven to be superior to both Admiralty and red brass in services where severe sulphide corrosion and dezincification are both encountered. It is also believed that a dual tube with an alloy of lower copper content for the outside shell, such as copper-lined Muntz metal, would be better on this type

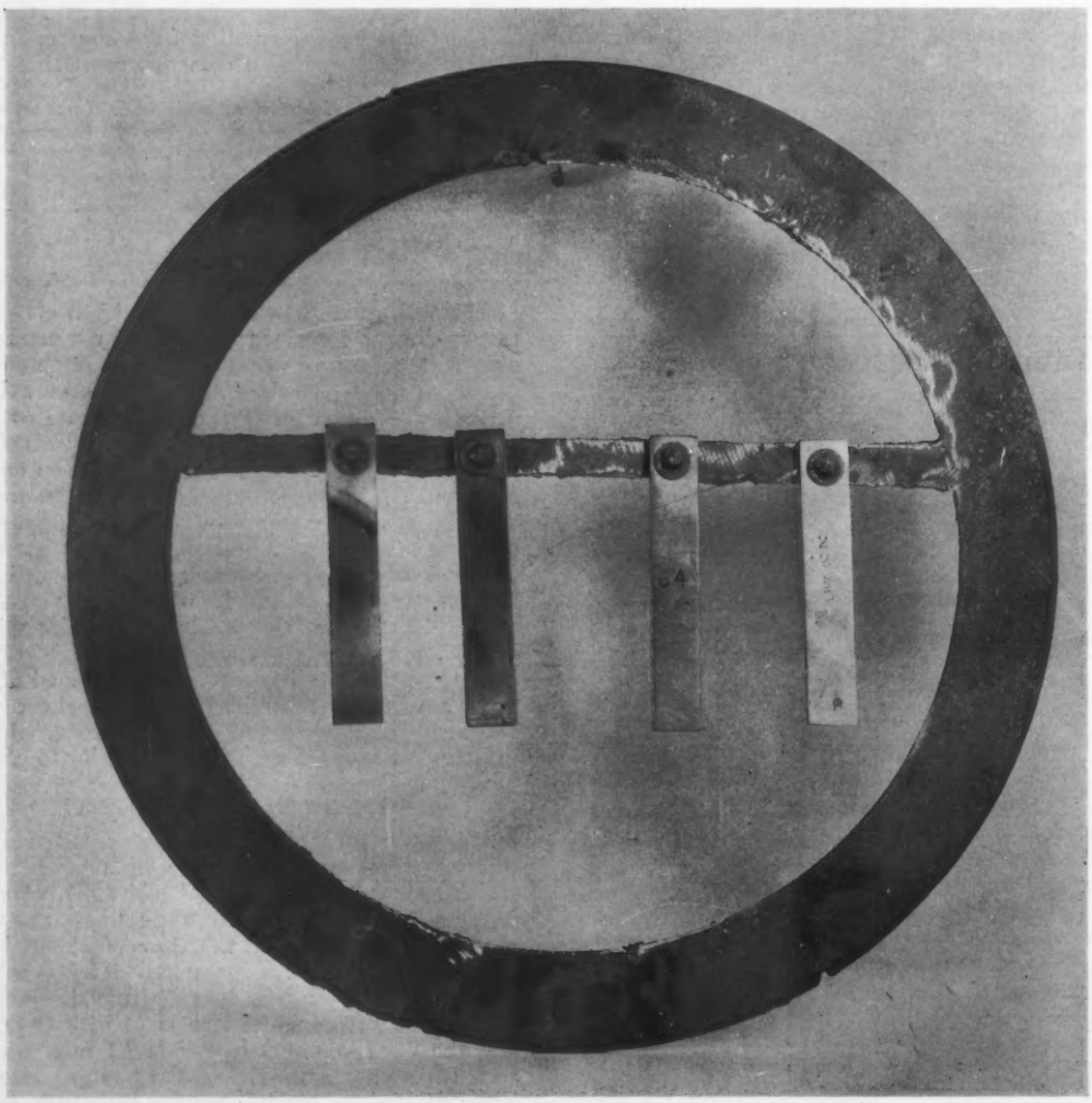


PHOTO 15845

of service than either red brass or copper-lined Admiralty would.

The copper-nickel (80-20) tubes showed early failures and were therefore not given any further consideration; however, one installation has given a long service after having been repaired several times.

The copper-nickel-tin metal gave fair service in a gasoline condenser but failed from water pitting. Additional tubes made of this alloy have been purchased for further tests.

One bundle of copper-nickel-zinc tubes gave excellent service in a gas-oil cooler, tubes being removed after 56 months service. Additional tubes have been purchased for further tests.

The other tubes listed in the tabulation—copper, copper-nickel-aluminum, arsenical Admiralty, red brass, with 1 percent tin, copper-nickel 70-30, and the three aluminum brasses are fairly new tubes on test, however, one bundle of the No. 1 aluminum-brass tubes has been on test for several years and we are buying approximately 2500 of similar analysis but of domestic manufacture for further tests.

Table 2 gives the approximate analysis of the different alloys on test.

Extensive records of the performance of the condenser tubes are kept, showing service conditions, life, etc. The attached chart, Table 3, is one record kept which shows graphically the relative life of several

TABLE 1
Comparison of Alloys in Water-Cooled Exchanger Service

Alloy	Cost	Life	Ratio of Life to Cost	Cause of Failure
1. Admiralty	1	1	1	Dezincification
2. Red Brass	1	1.5 to 3	1.5 to 3	Water pitting and oil corrosion.
3. Copper Lined Admiralty	1.5	1.5 to 3	1 to 2	
4. Copper-Nickel 80-20	2	1 to 3	0.5 to 1.5	Same as above.
5. Copper-Nickel-Tin	2.2	2 to 3	0.9 to 1.4	Same as above.
6. Copper	0.93	.....	.....	None to date.
7. Copper-Nickel-Aluminum	1.9	.....	.....	None to date.
8. Copper-Nickel-Zinc	2.16	*3	1.39	None to date.
9. Arsenical-Admiralty	1.3	Not installed to date.		
10. Red Brass with 1 percent Sn	1.5	Not installed to date.		
11. Copper-Nickel 70-30	1.67	Not installed to date.		
Al. Brasses				
12. No. 1 Brass	1.5	*3	2	None to date.
13. No. 2 Brass	1.4	.....	.....	Not installed.
14. No. 3 Brass	1.6	.....	.....	Not installed.

* Based on one installation only.

TABLE 2
Composition of Alloys on Test

Alloy	Copper	Zinc	Tin	Nickel	Aluminum	Arsenic
1. Admiralty	70	29	1	....	....	....
2. Red Brass	85	15	....	....	....	....
3. Copper Lined Admiralty	70	29	1	With Copper Liner.		
4. Copper-Nickel 80-20	80	....	....	20	....	....
5. Copper-Nickel-Tin	70	....	1	29	....	....
6. Copper	99+	....	....	....	....	....
7. Copper-Nickel-Aluminum	91.5	....	....	2.65	5	....
8. Copper-Nickel-Zinc	65	5	....	30	....	....
9. As. Admiralty	70	29	1	....	....	Trace
10. Red Brass plus Tin	85	14	1	....	....	....
11. Copper-Nickel 70-30	70	....	....	30	....	....
Al. Brasses						
12. No. 1	76	22	....	....	2	....
13. No. 2	76	22	....	....	2	....
14. No. 3	76	22	....	....	2	Trace

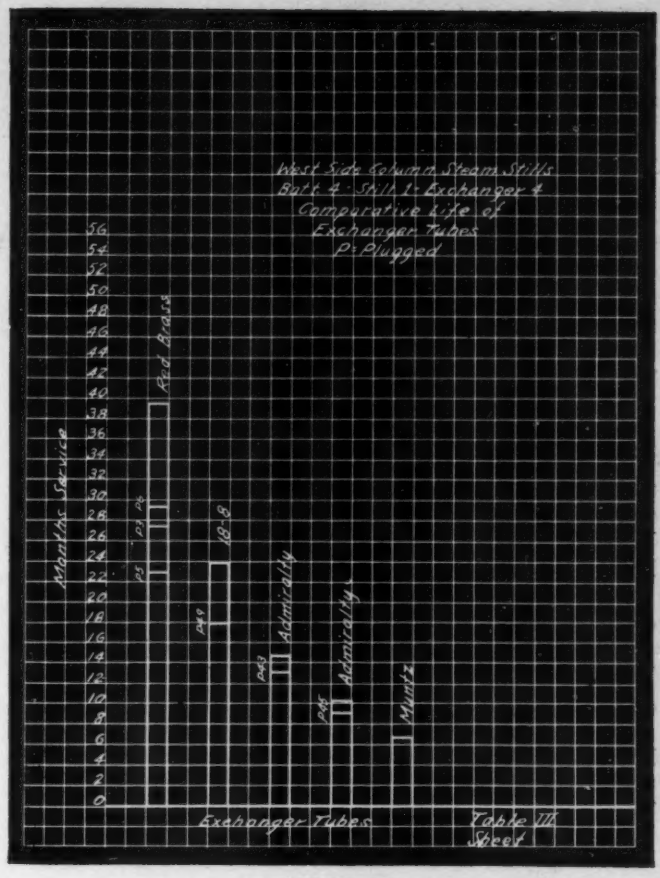


TABLE III

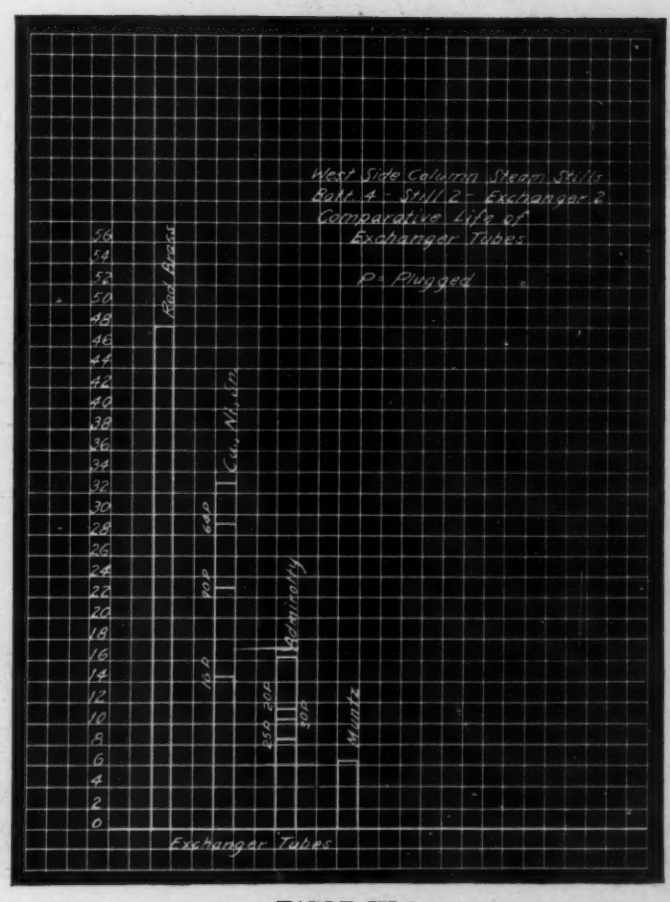


TABLE III-A

different alloys in one particular exchanger. In plant records each alloy is represented by a different color and the life of the tubes after repairs have been made is shown by cross-hatching. From this record the relative value of different alloys in a given service may be seen at a glance.

TREATING UNITS

Certain treating units, where sulphuric acid is used, must be built of materials resistant to sulphuric acid corrosion.

For transfer lines and for pumps, non-ferrous metals are satisfactory. Many copper base alloys have been installed. Some alloys are used such as aluminum bronze, copper-silicon-manganese, and lead for lines. Hard lead for valves, acid bronze for pump liners (85 percent copper, 10 percent tin, 5 percent lead).

For gate valves, nickel bronze is excellent; red brass and cast iron containing 12-15 percent nickel 5-7 percent copper, have shown merit in many cases; high silicon iron (85 percent iron 15 percent silicon) has been used but failure results from temperature changes.

For treaters, liners are customary—either lead liners or acid resisting brick liners. In general for lines and pumps the high copper base alloys are good. Red brass is not as satisfactory as other alloys used but it is cheaper and readily obtainable. Its use is quite general.

The following gives a description of one method of lining with lead.

Protection Against Sulphuric Acid Corrosion: Sheet lead is used in the oil refinery for the purpose of protecting the steel shell and roof of such vessels as agitators, mixers and separators from the corrosive action of the sulphuric acid normally used in treating operation.

The lead generally used is known as chemical lead. This is practically pure lead and derives its name from the fact that it is the type most widely accepted by the chemical industry. The chief characteristics of this material are that it is soft and that it has practically no elastic limit. The softness is a desirable feature because it means that the material can be easily worked into position in the vessel being lined. The low elastic limit, however, is an undesirable characteristic because it means that when the material is overstressed, as is regularly the case, the deformation becomes permanent. The lead eventually fails from cracking and not usually from the corrosive actions of the liquids being handled. The problem, therefore, is to utilize a stronger lead or to minimize the probability of cracking in chemical lead. Lead alloyed with antimony, tellurium or calcium gives a stronger material but one which is higher in first cost than pure lead. These alloys are more difficult to work and burn than pure lead and are not extensively employed in oil refinery operations. The latter two are still experimental and not advocated for routine service.

Sheet lead is specified and purchased on a basis of weight per square foot and not on a thickness basis as are most other metallic sheets. The thickness of a certain weight sheet is, of course known, but it is not the item considered when talking about sheet lead linings. Common weights of sheet used in the refinery are 6, 10, 12, 14 and 16 pounds per square foot. It is obvious, then, that the dead weight of this material constitutes

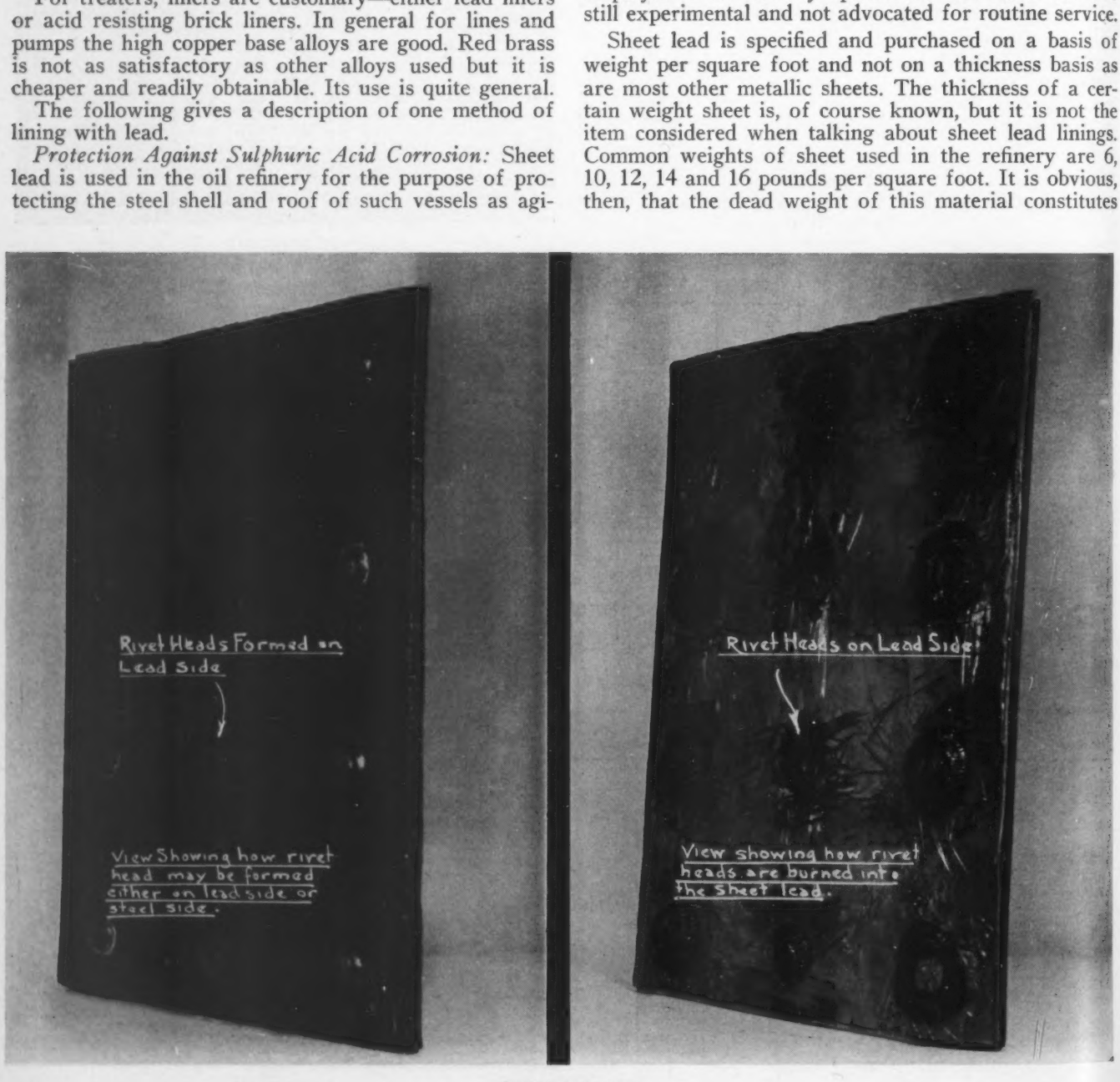

Rivet Heads Formed on Lead Side
View Showing how rivet head may be formed either on lead side or steel side.
Rivet Heads on Lead Side
View showing how rivet heads are burned into the Sheet lead.

PHOTO 19486

an important item for consideration. It is this dead weight plus temperature stresses which cause the ultimate failure of the lead lining.

The method of fastening the sheet lead to the walls and roof of a steel vessel is also a very important item for consideration. The method which has long been the standard is to use battens. The battens consist of half oval steel bars which clamp the lead to the steel plate by means of countersunk plow bolts. A narrow strip of sheet lead is then placed over the battens and the edges of this strip are then burned into the lead sheet of the lining proper. The best practice along this line, is to use only vertical battens and place them on about four foot centers. There is usually one circumferential batten where the shell lining joins the cone or bottom lining. The batten spacing on the roof and bottom of a vessel varies and depends on the shape of these parts.

The lead lining in an agitator is subjected to alternate heating—cooling cycles and also to mechanical vibration. If the acid bearing oil charged to the vessel is not already at a high enough temperature, it is further heated by means of steam coils. The oil is then agitated by means of jets of compressed air, introduced at the bottom of the vessel. The mixture is allowed to stand and settle before being pumped away. This heating—mechanical vibration—cooling cycle sets up stress in the lead sheet. The stress is naturally concentrated along the welds where the lead sheet is fastened to the vessel. Because lead had practically no lastic limit, it does not recover its original shape after undergoing these temperature stresses. The liner eventually fails by cracking along the welds. Cracks in the liner proper, between the lines of seams, have sometimes been observed.

Since chemical lead is generally preferred because of its low first cost and ease of workability, it has become necessary to find a more suitable method of fastening the lead in place than through the use of battens. The Texas Company has recently developed a method of holding the lead in place by using lead rivets instead of battens. The rivets are placed relatively close together and each one has to carry only a small load. Several installations are now about four years old and the indications are, that the lead rivet method requires less repairs than the batten method. In fact, no lead rivets have yet required any repairs. The lead rivets function equally well on the roof, shell or cone of a vessel.

The size of the rivet depends upon the thickness of the steel plate and the weight of the lead in question. For a 12-pound lead installation, a rivet having a 5/8-inch diameter shank, 1½ inches long and a 1⅛-inch diameter head 7/16-inch thick was used. On a 6-pound lead job, the rivet measured, 7/16-inch diameter shank, 1⅛-inch long with a head ⅞-inch in diameter and ¼-inch thick. The spacing of rivets on different installations has varied from 5 to 8 inches. The most economical spacing of the rivets has not yet been determined. The rivets are cast locally in homemade molds and are made from scrap lead of the same type as that used for the lining.

Photograph No. 19486 shows a specimen of steel plate which has been lined with sheet lead by means of the lead rivet method. The head of the rivet can be formed either on the lead side or on the steel side as shown. It is better practice, however, to form the rivet on the steel side because a more thorough job can be obtained and there is no danger of the rivet die cutting through the soft lead lining. A standard light weight pneumatic riveting hammer is used but the bucking-up tool must be especially recessed to accommodate the head of the lead rivet being handled. During the driving operation, the sheet lead liner is drawn up against the steel in the same manner as when riveting two pieces of steel together. The rivet head on the lead side is then scraped clean and burned into the sheet lead lining. There is no such thing as leaking around the rivet because it has been made homogeneous with the sheet. What has been produced, in effect, is a sheet lead liner having many small integral projections which have been inserted in holes in the steel plate, beaded over and thereby holds the lead liner in place. No lead rivet failures have yet occurred, but, it is anticipated that when they do take place it will be a case of simple shear fatigue failure of the shank of the rivet.

The relative cost of the lead rivet method has not been determined because all of the installations thus far have been of an experimental nature. It has been found, however, that once the steel plate has been drilled to receive the rivets, the work progresses faster and therefore more economically than it would if battens were used. The use of lead rivets makes possible a great reduction in the number of feet of lead burning required. The cost of using rivets on an existing vessel is slightly higher than it would be on a new one due to the fact, that in the first case, the rivet holes must be drilled on the job while in the second case, the holes can be punched in the fabricating shop during the operation in which the regular steel rivet holes are punched. This additional work is compensated for by the lower installation and maintenance costs secured through the use of a lead riveted liner.

In presenting this paper the author wishes to acknowledge the assistance of various members of the Engineering Department (Test and Records Department) of The Texas Company, and also to give credit as follows:

Figures 1 and 2, Curves 1, 2 and 3, Tensile Stress and Creep Data from Bureau of Standards Technical Paper 362 from Data by H. J. French, H. C. Cross and A. A. Peterson.

Figure 6, Long Time Creep Tests, from National Tube Data—Bulletin No. 20.

Extraction of Salts *from Refinery Stocks by the* Electrical Process

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WHILE the salt problem is not a new one to refiners, it is only within the past few years that it has become a factor of major importance in refinery operations. The increased emphasis now being placed upon the subject is due primarily to two quite unrelated factors, namely, the trend to higher temperatures and pressures in cracking operations and the increased use of acidizing in oil production. This discussion was presented before the Refinery Engineering Conference, Oil - World Exposition, Houston, Texas, October 15, 1937.

CHANGES in the design of cracking units have accompanied the increased temperatures and pressures now being used, with the result that the effects of coke deposition and corrosion have been magnified. The widespread use of acidizing, in addition to effecting the corrosive properties of the oil, has also resulted in the formation of additional salts in the oil, due to the reaction between the hydrochloric acid and the limestone formation.

As a result of these developments, the salt problem of today is much more far-reaching in its effects than the salt problem of five years ago. The refiner of yesterday was concerned with salt only insofar as it was responsible for mechanical stoppage of equipment. This trouble was usually remedied by washing the equipment with hot water or steam whenever the plant was shut down, and no particular preventive measures were taken. If the salt deposits were exceptionally severe, some relief could be obtained by water-washing the crude to reduce its salt content before it entered the system.

Today the refiner thinks of salt principally in terms of on-stream time and corrosion. He has learned that the lower the salt content of his charging stock the longer his on-stream time will be, for it has been demonstrated in many instances that the rate of coking is directly related to the salt content of the oil charged to the stills. This is well illustrated in the case of an Arkansas refinery processing a very corrosive crude of high salt content. The average length of run on a crude unit when the oil contained 100 grams of salt per barrel was between 3 and 6 days. Through the use of wash tanks, hot settling drums and other schemes for reducing salt content, runs were lengthened to 10 or 12 days. Following the installation of an electrical desalting unit, the salt was almost completely removed and runs of 60-70 days were normal.[1]

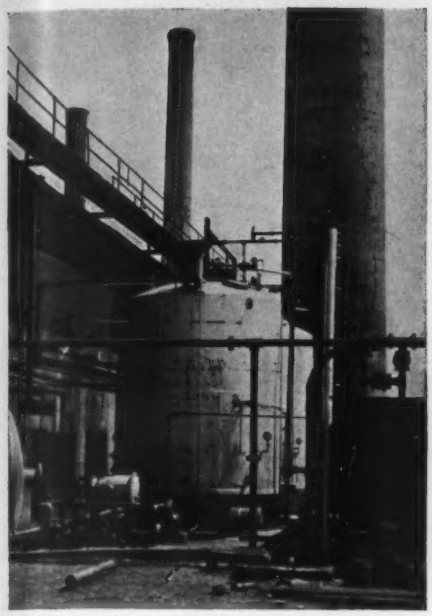
The refiner of today knows, too, that a large percentage of his corrosion may be directly charged to acids formed during refining by the hydrolysis of such salts as magnesium chloride contained in the oil being processed. One refiner is quoted as saying: "Corrosion is directly proportional to the amount of salts in the crude. The rate of corrosion is proportional to the kinds of salts in the crude."[2] A good example of the relationship between salt content and corrosion is reported in connection with the Arkansas refinery referred to above. During normal operation of the refinery, samples were taken before and after the oil had passed through the desalting units. The untreated oil, which contained 107 grams of salt per barrel, showed a release of 63.83 pounds of HCl per 1000 barrels of crude, while the desalted crude, containing 5.6 grams of salt per barrel, released only .54 pound of HCl per 1000 barrels.[1] In other words, a 95 percent removal of salt reduced the formation of HCl by 99.5 percent.

Another illustration of the relationship between salt content of charging stocks and corrosion is found in the seasonal variations in both salt content and corrosion. One case is cited where the salt content of a crude oil ranged from 20 to 30 grams per barrel in summer to 120 grams per barrel in winter. At this refinery only normal corrosion was experienced during the summer months, while it became a serious problem during the winter. Another refiner reported an average of 14 pounds per 1000 barrels in summer as compared to 60 pounds per 1000 barrels in winter.[2] The seasonal difference in salt content is attributed to the faster and more complete settling of salts and residual brine in storage during hot weather.

As a result of the increased corrosion in cracking and topping units in Kansas, Oklahoma and North Texas refineries, it is reported that processing costs have risen from a fraction of a cent to as high as 3 cents per barrel of crude charged.[2]

As the troubles due to salt have become more serious, refiners have taken measures to counteract its effects. Considerable advancement has been made in combating corrosion of refinery equipment through the use of new corrosion-resisting alloy metals. Neutralizing agents are also being used to advantage. But, these measures do not attack the problem at its source and attention has been directed to methods for the removal of the salt before it enters the refinery. More complete dehydration of crude oil emulsions in the field through the imposition of stricter pipe line requirements has helped.

In many districts .5 percent b.s.& w. is the maximum allowable emulsion content. It is not generally realized, however, that even this small percentage



One of the first electrical de-salting plants installed in an Arkansas refinery, reducing the salt content of crude charged from approximately 120 grams to between 1½ and 3½ grams per barrel.

of brine can carry large amounts of salts in solution. For example, 10,000 barrels of oil containing .5 percent of oil field brine of average salinity may easily contain 2500 pounds of salts, all of which are dissolved in this relatively small volume of water.

Washing methods have been employed with some degree of success. Simply washing the crude through hot fresh water does not give very satisfactory results, so means are usually taken to bring about a more intimate mixture of the salty crude and the water, with resultant increase in separation difficulties. The efficiency of such methods, however, is limited, and it may be said in general that the most efficient processes of this type have a maximum efficiency of about 70 percent.[3] As it has been demonstrated that corrosion and stoppage may be encountered in cracking equipment even when the salt content of the charging stock is as low as 10 grams per barrel, it will be readily seen that a 70 percent extraction would not be sufficient to prevent corrosion and stoppage when handling oils of high salt content.

Recent reports indicate that advances have been made in the utilization of salt settlers that operate under considerable heat and pressure, but it is understood that the operation of such equipment is very critical as to throughput rates, temperature limits, etc.

A good illustration of the difficulties that may be experienced in handling oils of relatively low salt content is given in the case of a Gulf Coast refinery operating on a mixture of East Texas and Louisiana crudes. Although the salt content of the crude averaged only 14 grams per barrel, considerable trouble was experienced with corrosion and mechanical stoppage of heat exchanger tubes. Electrical desalting of the crude made the difference between satisfactory and unsatisfactory operation at this refinery. An electrical desalting plant reduced the salt content to between 1 and 2 grams per barrel, thereby eliminating the stoppage trouble. Ammonia requirements were reduced from 25 pounds to 1 pound per day. There will probably be no further corrosion of the equipment used in the first stages of distillation. The effect of salt removal on the corrosion of secondary distillation equipment remains to be seen.

Another refiner running on East Texas crude not only experiences corrosion and stoppage with 10 grams of salt per barrel, but also got a charge of salt into some finished lube stock which was not discovered until the customer returned it. This salt had apparently accumulated in the trays of the bubble tower and carried over into the lubricating oil mechanically.

In the past six months numerous severe cases of corrosion have shown up in refineries running East Texas crude. These plants have experienced the usual chloride corrosion in their primary distillation, and in addition to this have encountered unexplainable corrosion in cracking equipment. This corrosion occurs not only in equipment cracking raw crudes, but also in systems cracking gas oil. It is interesting to note that this trouble did not appear until this crude began showing salt water.

The removal of salts that hydrolyze to form HCl

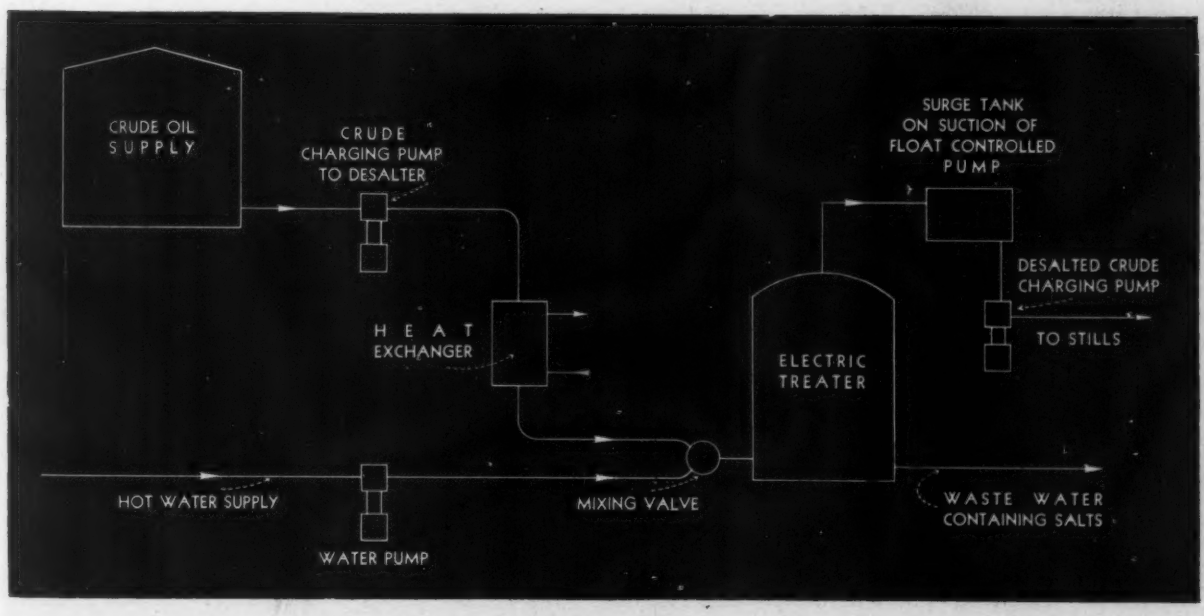


FIGURE 4
Flow chart of the electrical desalting process

is especially important when refining sulphur bearing crudes, as it is well known that corrosion trouble due to CH1 is increased in the presence of hydrogen sulphide.

It was because of the demand for a more efficient and rapid process for salt removal that the electrical process was introduced. This method eliminates many of the disadvantages inherent in systems formerly used, one of the principal advantages being that it can be incorporated into the refinery system in such a manner that the charging stock can be almost completely desalted and returned to the system without the heat losses that accompany processes involving prolonged settling periods. The process and equipment employed are covered by issued and pending patent applications in the United States and foreign countries.

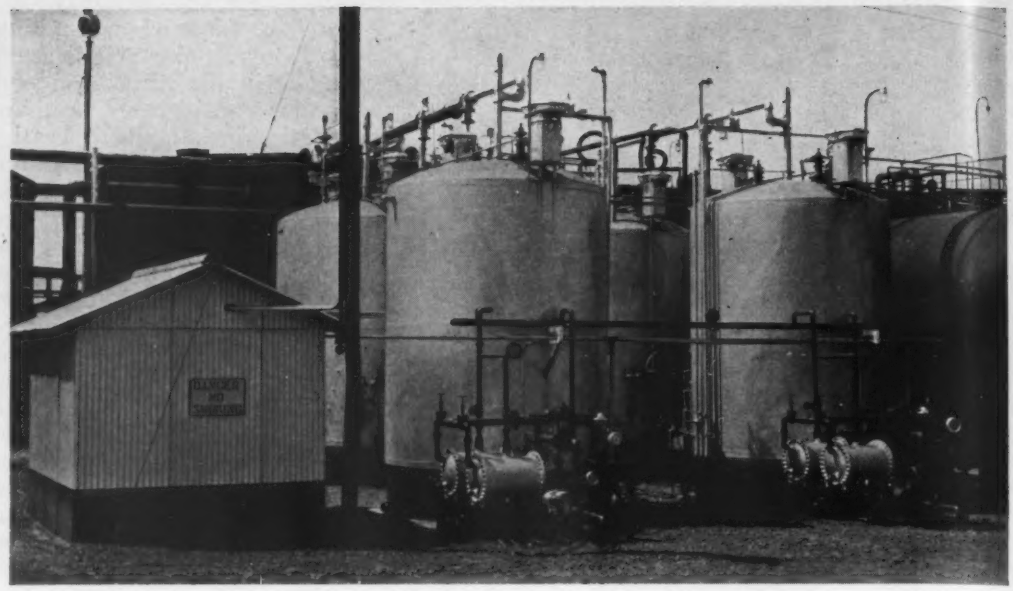


FIGURE 2

A four unit electrical desalting plant which has been operating in an Arkansas refinery for over a year.

The fundamentals of the process used are relatively simple and consist of three principal steps, as follows:

(1) Fresh water is added to the oil stream, the oil and water being passed through a mixing device. This is usually done after the oil has passed through the first heat exchanger at temperatures ranging between 140° and 190° F. There are various ways in which the water may be incorporated into and mixed with the oil, but best results have been obtained by pumping the required amount of water (usually between 5 and 50 percent by volume) into the oil stream and then passing the stream through a properly controlled mixing valve. The most desirable pressure drop across such a mixing valve varies with different oils. The control of the mixing step is one of the most important phases of the process and must be properly correlated with the subsequent action which takes place in the electric field.

(2) The mixture after passing into the electric treater is subjected to the action of a high voltage electric field which serves to treat it and coalesce the water particles until they become large enough to gravitate from the oil. The use of this electric field results in the removal of 90 to 95 percent or more of the salt with the water. Comparative tests show that a much higher proportion of salt is extracted in this manner than when the mixture is separated by other means.

(3) The coalesced water masses are permitted to separate by gravity from the now-purified oil and form a body of water at the bottom of the treater which contains the salts previously present in the incoming oil. This water is continuously removed from the bottom of the treater, and the separated desalted oil leaves the top of the treater and continues through the refinery system.

An electrical desalting plant usually consists of two or more standard sized units, the number depending upon the volume of oil to be treated. The multiple unit system has proven the most flexible and economical. Single unit plants may also be used where the volume of oil to be handled is not too great. In general, it may be stated that a single unit will treat about 1500 barrels of oil per day, although single unit plants operating in Michigan have handled as high as 2800 barrels of high salt content oil per day with an extraction of over 90 percent. Units operating on East Texas crude have treated as high as 2500-3000 barrels per day.

The electric treater proper consists of a pressure vessel 10 feet in diameter by 12 feet in height, and is designed to meet A.P.I.-A.S.M.E. specifications for 35 pounds working pressure. In this container are suspended two or more suitably insulated electrodes which form the treating field. Special step-up transformers are positioned on top of the treater tank, and are supplied with alternating current at 230 volts. The requisite high potential is conducted through the treater shell to the electrodes by means of an entrance bushing. Transformers rated at 5 K.V.A. giving potentials of about 16,500 volts are commonly used in desalting procedure, and when two transformers are employed on a single unit, as is usually the case, the circuit is so designed that the high tension side of each transformer is connected to one of the electrodes. The polarity of the transformers is so arranged that when connected in this manner there will be a potential of 33,000 volts between the electrodes, but only 16,500 volts from each electrode to the grounded treater shell. This results in localizing the maximum voltage in the treating field, where it is needed, and simplifies the problem of electrical insulation.

Reactance coils control the power going to the transformers, and an automatic switch controls the power to the unit. Should the liquid level within the treater tank be lowered for any reason, the power is automatically cut off. Electricity can be delivered to the electrode system only when the treater is full of liquid.

The salt removing efficiency of the electrical desalting process depends to a considerable extent on the type of electrode employed and the manner in

which the oil-water mixture is injected into the high voltage field. The type of electrode particularly applicable to desalting service consists of a number of vertically extending concentric rings of ribbon steel, held together by a suitable framework and disposed in a horizontal plane in the treater. Two of these electrodes ordinarily are employed, one being positioned directly above the other.

In most instances it has proved particularly effective to inject the oil directly into the electric field before any separation or sludging of the constituents can take place.

One method commonly used is to discharge with considerable velocity from a distributor, positioned in the center of the treater tank midway between the electrodes, in such a manner that the incoming mixture is caused to flow radially outward in a thin stream into the treating field. Thus, all the incoming fluid must pass directly through the electric field. The electric field is useful not only in forming droplets of sufficient size to gravitate from the oil to effect separation, but it has been found that some unexpected action takes place therein which facilitates incorporation of the salt into the water which is settled out in the treater.

The process is continuous and requires no extra labor. Operators inspect and regulate the treaters the same as they do other units in the refinery.

Aside from a nominal license fee, the principal factors entering into the cost of operation are water, heat and power. When refinery waste water is utilized, as is usually the case, water costs are negligible. Most refiners do not charge heat directly against the cost of desalting, due to the fact that no additional heat is required unless it is necessary to raise the temperature of the wash water. This may be accomplished by utilizing exhaust steam.

The electric power actually chargeable to the desalting unit is low, usually averaging less than 48 K.W.H. per day per unit. A unit processing 1600 barrels per day would thus average about 30 watt-hours per barrel.

The only other operating expense is the cost of pumping the desalted oil back into the system. Overall operating costs, including license fee, have been found to range between 0.75 cents and 1.2 cents per barrel, depending on the amount of oil treated.

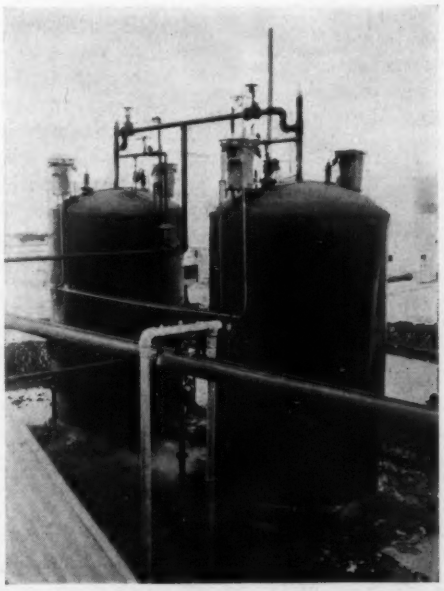
The principal benefits resulting from the operation of electrical desalting plants installed to date have been:

(1) Increased on-stream time.

(2) Decreased corrosion.

(3) Improvement in refined products.

On practically all plants installed to date, runs have been increased to about five times the best previous record. In two cases there were increases of 1000 percent. One refinery in Arkansas increased its maximum on-stream time from 6 days to over 60 days, and a Michigan refinery increased its best continuous run record from 12 days to 120 days.



A two-unit electrical desalting plant installed in a Kansas refinery handling approximately 2,500 barrels a day with salt removal efficiency of over 90 percent.

The cost of shut-downs is an important item of expense under any conditions, but on-stream time is of especial significance to refiners under the market conditions prevailing today.

Figures on shut-down expense furnished by several different refiners indicate a cost varying between 30 and 60 cents per barrel throughput for every shut-down. For example, one refiner running 8500 barrels of mixed crude per day estimates that shut-down time costs $5000 per day. This refiner figures that even though salt is not present in sufficient quantities to cause mechanical stoppage of equipment, the risk of shut-down, due to the corrosion of equipment, is so great that the use of the electrical desalting process is justified, especially since it is necessary to desalt only half of the throughput. Another refiner running 3000 barrels of East Texas crude per day estimates the cost of shut-down time at over $1000 per day, while a third refiner whose principal product is asphalt processes 5000 barrels of crude per day and estimates that shut-down time is costing $1800 per day.

Although it is definitely known that salt removal will be reflected in less corrosion of refinery equipment, it is as yet too early to present any data on the effects of electrical desalting on corrosion, as these costs can only be figured over extended periods. It has been proven, however, that an efficient desalting process materially reduces the formation of acids responsible for corrosion.

The principal effect of desalting upon refined products is found in residual products, particularly asphalts and road oils, in which the allowable percentage of insoluble material, such as salt, is limited. In one case a refiner was unable to meet a 99.5 percent solubility requirement on his asphalt. As a result of electrically desalting his charging stock, the solubility of his asphalt was increased to over 99.9 percent.

That there is a need for an efficient method of salt removal in refineries, and that the electrical process is meeting the requirements, is evidencd by the fact that in the past two years 48 units have been installed and 15 more units are now on order awaiting fabrication and delivery of material. These units are located at 15 different refineries in various sections of the Mid-Continent area. The applicability of the process to a wide variety of oils ranging from 18° to 42° A.P.I. and with salt contents as low as 14 grams and as high as 300 grams per barrel has already been demonstrated.

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Laboratory Equipment and Methods for

Testing Lubricating Greases

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Battenfeld Grease & Oil Corporation

EVEN though increased interest has been manifested in recent years, the paucity of standard and tentative standard methods for testing lubricating greases has handicapped both the manufacturers and purchasers. The latter have particularly needed uniform methods which could be referred to in proposals for bid and used in checking samples or actual purchases.

The old time grease manufacturer did not maintain a laboratory and left the matter of physical characteristics of the finished lubricating greases entirely to the grease maker who generally did a surprisingly good job. Then, too, there was a great deal of secrecy about the business, with each company feeling its process or processes different and better. The truth is that all manufacturers have always used about the same methods for making the various types of greases, and in these days of excellent laboratories and skilled chemists if something new is brought out, it is not long before others are cognizant of the composition and properties.

The grease maker was inclined to resent the intrusion of the chemist in his business, but when he learned it meant better control of uniformity and helpful advice on the chemical reactions involved, his attitude changed. It seems quite apparent that there always has been and always will be an art in making grease, no matter how much the equipment is improved. Thus, the ideal combination is a grease maker of long experience working with skilled chemists who have a well equipped laboratory.

The changing attitude of the grease manufacturer has made all realize that standard methods of test are needed, not only for best plant control but also to insure the consumer getting satisfactory products no matter where purchased. Another very important point is practically eliminating disputes which may often be costly, between seller and purchaser, due to both using exactly the same testing methods.

At present the Methods of Analysis of Grease (D128-27)[1] and Tentative Method for Penetration of Greases and Petrolatum (D217-33T)[2] are the only ones which have been approved by the American Society for Testing Materials for the testing of lubricating greases. This year the following method covering determination of dropping points (so-called melting points) of lubricating greases was published for information and trail, before advancing it to the tentative standard basis.

Sub-Committee IV on grease of Committee D-2 of the A.S.T.M. has also been giving consideration to determining the consistency of soft lubricating greases. They cannot be accurately tested on the present grease penetrometer where the penetration is over 390-400. The MacMichael Viscosimeter has found favor in certain laboratories but its accuracy is limited for some types of greases. A modified Gardner Mobilometer seems to have been most acceptable and it is hoped samples can soon be circulated to those having the apparatus so comparative test figures can be obtained. At least one laboratory supply company has listed the modified Gardner Mobilometer in its catalog.

The present method for determining the amount of water in grease (Methods of Analysis of Grease D128-27) does not give accurate results due to glycerine being carried over with the water. A method which eliminates that fault has been circulated to members of Sub-Committee IV. Since the above methods were approved in 1927, other revisions may soon be advisable to bring them in line with changes which various grease laboratories have found to improve speed and accuracy.

With the Grease Penetrometer (D217-33T) the consistency of small quantities of lubricating greases cannot be determined and that is often desirable where small samples only are available. An attachment which will enable it to be done is being considered and tested. Results obtained will be correlated with those obtained on the standard apparatus so a table can be prepared which will enable easy correction of tests to correspond to use of the regular Penetrometer.

The Grease Worker prescribed in the above method for penetration of greases is being revised. That will make it easier and quicker to use, more sturdy, and also provide enough grease after working to smooth off and take the penetration directly in the Worker. That is hardly feasible with the present apparatus. The Penetrometer itself has been voluntarily improved by one laboratory supply company. The present model is quite different in appearance from the old asphalt penetrometer originally used in operation of the cone. It also permits easier handling and closer checking of samples.

It is hoped to shortly develop laboratory control tests for channeling of gear lubricants and their tendency to foam in use. These, of course, to be correlated with actual service tests so they will be of practical value. The increasing use of hypoid gears makes such tests highly desirable because such gears can quickly be ruined if there is channeling of the gear lubricant in cold weather.

Obviously progress in the work of Sub-Committee IV is slow due not only to the number of members, which is now 20, but also because all methods considered must be checked and double checked as to value and accuracy before they can even be submitted for consideration as tentative standards. In that status they remain under the guiding hand of the Sub-Committee until advancement to a standard method. Even then revisions can be made if they become necessary.

Bearing manufacturers have not been entirely satis-

*Presented before the Fifth Annual Convention of the National Lubricating Grease Institute, Chicago, October 4 and 5, 1937.

Proposed Method of Test for Dropping Point of Lubricating Greases[1]

This is a proposed method and is published as information only. Comments are solicited and should be addressed to the Headquarters of the Society, 260 S. Broad Street, Philadelphia, Pennsylvania.

1. **SCOPE**—This method is intended for use in determining the dropping point of lubricating greases.

2. **APPARATUS:** (a) **THERMOMETER**—The thermometer shall be graduated in Fahrenheit degrees, the range being 20 to 580° F., and shall conform to the Standard Specifications for A.S.T.M. Partial-Immersion Thermometer for General Use (A. S. T.M. Designation: D 183) of the American Society for Testing Materials.[2]

(b) **GREASE-CUP ASSEMBLY** — The grease-cup assembly shall conform to the requirements shown in Figure 1.

(c) **ACCESSORIES**—Accessories required consist of a test tube approximately 4 cm. in diameter by 18 cm. in height, a 600-ml. beaker, ring stand, clamp for test tube, support for beaker, gas burner, suitable oil[3] for oil bath, etc.

3. **PROCEDURE**—(a)—The grease-cup assembly shall be placed in position on the thermometer at a height so that the tip of the thermometer bulb will be 1/8 inch above the bottom of the grease cup, **A**. The set screw, **B**, shall then be tightened to hold the assembly in position on the thermometer.

(b) The grease cup shall then be removed and filled with grease by pressing the larger end into the grease to be tested until the cup is filled, taking care to avoid inclusion of air. Working the grease shall be avoided as far as possible. Excess grease shall be removed with a spatula or knife.

(c) The full grease cup shall then be placed on the retaining ring, **C**, and the ring screwed in position to bring the thermometer bulb to the original position with respect to the cup outlet. Grease forced out in this operation shall be carefully removed.

(d) The thermometer and assembly shall then be placed in the test tube with the bottom of the cup 1 inch from the bottom of the test tube and the test tube suspended in the oil bath submerged to one-half its height.

(e) The oil bath shall be heated so as to cause the temperature indicated by the thermometer to rise at a rate of 8 to 10° F. per minute until a temperature approximately 30° F. below the expected dropping point of the grease is reached. At this point, the rate of heating shall be changed to 2 to 3° F. per minute. As the temperature increases, grease will gradually protrude through the orifice of the grease cup. When a drop of grease falls, the temperature shall be noted and recorded as the dropping point.

NOTE—The dropping point as determined by this method gives information as to when softening begins under the conditions of the test, but should not be considered as having any bearing upon performance in service.

[1] Under the standardization procedure of the Society, this proposed method is under the jurisdiction of the A.S.T.M. Committee D-2 on Petroleum Products and Lubricants.

[2] 1936 Book of A.S.T.M. Standards, Part II, p. 1405.

[3] A suitable oil is one that does not vaporize appreciably at the temperature of the test and does not darken rapidly with repeated heating. Castor oil is satisfactory.

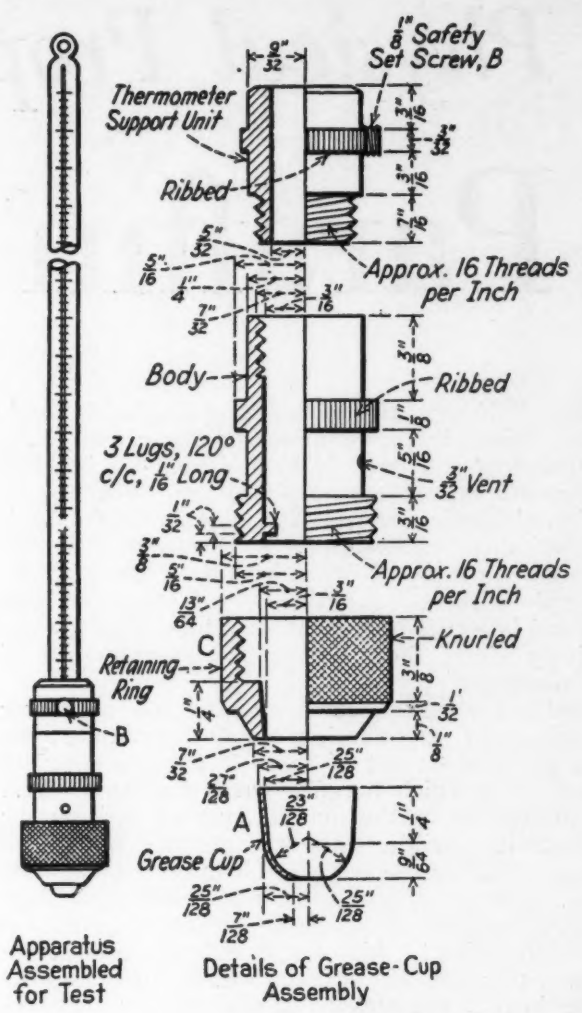

FIGURE 1

Apparatus for Testing Dropping Point of Greases.

When assembled for test, the lower end of the bulb shall be placed exactly 1/8 inch above the bottom of the grease cup.

fied in the past with lubricating greases supplied them or used on bearings by their customers. That, in part, led to the formation of a committee with representatives from each cooperating manufacturer, known as the Bearing Engineers' Committee. This committee has developed an apparatus known as the B.E.C. machine for testing greases on actual bearings. The characteristics of the greases are determined before and after running on the machine. The changes are indicative of what can be expected of the grease in service. It is hoped that a correlation of the results on the machine with use of the various bearing greases over a period can be effected. That would make it a valuable addition to the laboratory of the manufacturer of lubricating greases. There is general agreement that better bearing greases are needed, especially for the wheels of automobiles. Dragging brakes, tight fitting bearings, and other mechanical difficulties which can come up make it a tough problem.

The so-called oxidation of lubricating greases has caused plenty of grief, particularly to manufacturers using either roll or ball bearings. This applies especially to those who make equipment where bearings have been packed which may not be placed in use for months or years. If the grease has deteriorated, the bearings may soon be burned out when the machinery is finally operated. Those manufacturing electric motors have particularly been sufferers along that line. That condition has stimulated work on a method embodying an accelerated stability test which could in the long run be found to closely simulate the above storage conditions. One has been developed by F. L. Wright and W. A. Lutz,[3] which gives much promise and the apparatus needed has recently been made available by one of the laboratory supply companies.

B. B. Farrington and W. N. Davis[4] have studied the texture and structure of lubricating greases by means of photomicrographs taken with dark field illumination. The length of the soap fibre was found to vary con-

(*Continued on page 475*)

STUDIES ON THE

Physical Properties of

Paraffin Wax

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PARAFFIN wax, an interesting and valuable product obtained in the refining of many crude petroleums, was first discovered by Reichenbach in 1830, by means of the microscope, as a solid structure in a cooled alcoholic solution of crude oil. Reichenbach published these observations in the same year but they were only of scientific interest. However, the studies about these important observations have been continued by other investigators, which after a comparatively short time led to the manufacture of paraffin wax.

Petroleum when refined is separated into a number of fractions by vaporization and fractionation. One of the most important of these is a lubricating oil fraction from which paraffin wax, if present, must be removed before the manufacture of satisfactory lubricants is possible. This removal may be carried out when cooling the paraffin oil under proper conditions. In this process the wax particles crystallize, and may be filtered through presses. One of the major difficulties in this operation is the production of proper paraffin wax crystals which can be rapidly filtered through the presses. In other words, different types of wax crystals are to be found in the paraffin wax distillates. The crystalline behavior and chemical composition of paraffin waxes found in different crude oils have been sources of much discussion, and a number of conflicting theories have been advanced to explain their composition or crystalline peculiarities.

In the early days of the oil industry it was thought that paraffin wax existed in two forms, the first form being amorphous, the second having a crystalline structure. According to this opinion, only the amorphous form of paraffin wax was dissolved in the crude oil. It was believed that the distillation process was able to transform the amorphous form into the crystalline structure. Zaloziecki, the Polish investigator[1], was the first to find that both crystalline and amorphous waxes are present. To prove these observations, Zaloziecki treated waxy residue of Klenczany crude oil five times with amylic alcohol—that is to say, he extracted certain higher molecular hydrocarbons. As a result, a crystalline paraffin wax was obtained with a melting point of about 59° C. He therefore postulated the theory that amorphous waxes (protoparaffins), probably branched chain, were converted into crystalline waxes (pyroparaffins), straight-chain hydrocarbons by distillation. However, this simple distillation leads to a decomposition of certain hydrocarbons, causing a reduced viscosity in the mother liquor.

It is true that the preceding work executes a destroying of crystallization inhibitors and reduces the viscosity of the mother liquor, but at the same time it causes the decomposition of higher-melting paraffin waxes into lower-melting waxes and gas. Further, the decomposition of the mother liquor deteriorates its oiliness, resulting in the impossibility of manufacturing lubricating oils of high quality. Gurwitsch[2], studying the crystalline behavior of petroleum waxes with the aid of a petrographic microscope and polarized light, found that those which had not been distilled or recrystallized by solvents were crystalline. His conclusions were that Zaloziecki's amorphous paraffin wax was not actually amorphous, but that the crystalline development had been retarded and altered by the crystallizing medium or oil, and possibly by the presence of colloidal material.

Many investigators have substantiated that the crystallizing medium and the presence of colloidal material do influence the behavior of petroleum waxes. They concluded that some crystallization inhibitors are adsorbed on the surface of the minute wax particles, increasing their surface tension. This causes them to become surrounded by a protective film of oil which prevents the ready growth of the crystals. The tar and resin-like substances act as inhibitors. In other words, after removal of these inhibitors the paraffin wax particles should crystallize.

However, it has been stated by many investigators that there are also wax crystals which make great trouble during the removal of paraffin wax from wax distillates. Rhodes, Mason and Sutton[3] maintained that there are two types of crystals, needles and plates, and the needles are formed from the plates. Buchler and Graves[4] stated that the purified paraffin crystallizes in plates and the wax containing impurities produces needles. Graves[5], in another communication, claimed he had obtained crystallized plates entirely from purified paraffin wax. Again Ferris, Cowles and Henderson[6] found three broad types of crystallization, viz., plate, needle and malcrystalline, in purified paraffin obtained from a Mid-Continent petroleum. This indicates that all these states are the consequence of different inhibitors, which influence their formation. A method which is

able to remove the inhibitors from the wax distillate fraction is the pipe still process. Here an exact fractionation between hydrocarbons and inhibitors of tarry or resin-like nature is accomplished. The inhibitors are condensed in the bottom of the fractionating tower, while the paraffin-wax distillate leaves the tower as vapors, being condensed in water-cooled condensers or heat exchangers. This process may be considered as more economical, because of large yield of good quality paraffin wax and lubricating oils. But this process encounters other difficulties. The mother liquor of the wax distillate obtained shows too high a viscosity to allow proper crystallization of wax particles.

Especially the slop-wax distillate fraction over 0.895/15° C. gives considerable trouble in the matter of separation of paraffin wax from oils. This shows that viscosity of the mother liquor influences crystal size; that is, the more viscous the liquor the smaller the crystals. Of course, the velocity and time of cooling also influence the size of crystals. The more rapid the rate of cooling of a given wax distillate the smaller the crystals obtained. Again, the more concentrated the solution of paraffin wax the smaller the crystals. Dilution of a high-viscosity wax distillate in gasoline aids crystallization of wax particles, but such a diluted mixture gives a great deal of trouble in paraffin wax separation. The reason for this is that the paraffin wax crystallizes in this solution in the form of plates, and since the plates lie compactly, the oil flows slowly when the wax distillate is pressed.

The success of filter-pressing depends not only upon the growth of crystals, but also upon the form of crystallization. Preferably they should be in the form of needles rather than plates, because the former results in a more porous cake through which the oil filters more readily. The highly-viscous distillate diluted with gasoline shows a growth of plates, but the growth being very compact, the oil runs out slowly when the wax distillate is pressed.

According to the writer's investigations, the heavy wax distillate contains certain highly-complicated hydrocarbons that prevent the transformation of the plates into needles. It was stated that a paraffin-wax particle in a heavy wax distillate is surrounded by two protective films, the first exterior film containing a tarry or resin-like substance, while the second interior film, which is in direct contact with the paraffin wax particle, consists of certain highly-viscous hydrocarbons. When a wax particle is surrounded by these two films, they cause the particle, on account of their high surface tension, to be in amorphous form. After removing the first film the tension decreases to a certain degree, causing growth of crystals in the form of plates.

Extraction of the second film causes the entire disappearance of the surface tension, allowing the paraffin wax particles to crystallize into needles. These phenomena play a very important part in the manufacture of paraffine wax, because a bad crystallization gives trouble, especially during the sweating of press paraffin concentrate, a process based upon the successive raising of temperature in the sweating chamber, until a successive or fractional melting or sweating of the higher melting point paraffin takes place.

Paraffin-wax concentrate (the so-called slack wax) contains about 50 percent of the mother liquor. This paraffin-wax concentrate is composed of a mixture of various individual paraffin-wax particles in the oil. Should the oil of this concentrate consist of the inhibitors of the first and second film, the crystallization of the paraffin wax particles will be in proportion. When therefore, in the first stage of the sweating process, melted paraffin concentrate is allowed to cool off in sweat pans, the needles crystallize out first, then the plates, and finally the particles in amorphous form; however, the crystallization would not occur in layers but irregularly, because all particles are intimately mixed. The needles are broken by the plates, and large proportion of plates are dissolved in the colloidal paraffin particles. With continued lowering of temperature considerable oil with dissolved paraffin particles of amorphous structure would leave the chamber, dissolving a great number of plates on their way.

When the temperature of slack wax is allowed to rise slowly and evenly, the separation results in wax-free oil, all wax particles being crystallized as needles. In this instance the separation of the needle crystals and the oil takes place during the cooling of the concentrate. The oil lies freely between the needle structure and when the concentrate is warmed it flows down through the skeleton of the needle structure, leading to a formation of a paraffin wax skeleton free of oil. Against that the concentrate with developed plates or broken needles reveals other properties; during the sweating process the sweating oil dissolves many of the paraffin-wax particles. This phenomenon may be compared to a baffle that holds back the sweat oil, thus preventing a rapid run-off. It can be seen from the above that the concentrate with the developed plates and amorphous particles cannot be submitted to a sweating process.

It must be first recrystallized by repeated cooling. This results in the wax crystals being in better condition than the original concentrate. Following this process the wax particles lie loosely packed so that the concentrate obtained is comparatively easier to sweat. There are also certain advantages connected with slow cooling of a mixture of oil and wax from a high initial temperature. High temperature makes the oil less viscous and allows crystals to form in better conditions, because the inhibitors can flow through the press cake together with the filtrate. This process also presents many disadvantages; a high yield of filtrate rich in paraffin wax as colloidal and plates results. This so-called "secondary filtrate" must be mixed with the primary wax distillate to be partly recrystallized under high pressure in the cold press. It can be seen from the above that the two half products such as sweating oil and the secondary filtrate give trouble in the manufacture of paraffin waxes. This procedure may be therefore considered very inconvenient because a great deal of wax must be recooled and recrystallized.

In consequence, the initial wax distillate will consist of 100 parts ordinary wax distillate, 40 parts filtrate obtained from the recrystallization, and 10 parts sweating oil. It is necessary to find out proper conditions whereby the wax particles crystallize as needles. For this purpose a proper dilution of mother liquor and absence of inhibitors are essential. The heavier the cut, the more viscous the mother liquor and the greater the proportion of the inhibitors. First distillation cuts show a very good dilution and absence of inhibitors. Therefore it is convenient to collect three fractions during the distillation process of crude oils, whose mother liquors show quite differ-

ent characteristics. The first fraction 0.845-0.870/15° C. has a lower viscosity and is free from inhibitors. This fraction allows wax particles to crystallize into needles, and thus can be easily crystallized, filtered and sweated. The other two fractions, however, show quite different characteristics. The second fraction, 0.870-0.895/15° C. contains a mother liquor of higher viscosity, causing the wax particles to crystallize into plates. It can be crystallized and filtered, but sweating of the slack wax gives trouble. The third fraction, 0.895-0.940/15° C., with a mother liquor of very high viscosity and a large proportion of inhibitors of tar and resin-like character causes wax particles to remain in the amorphous form. Therefore it can be neither pressed nor sweated. These various crystallization characteristics show that each of the above mentioned cuts should be treated differently.

The first fraction can be easily dewaxed. The initial operation thus consists in cooling this wax distillate to about — 6° C. The oil is transferred to

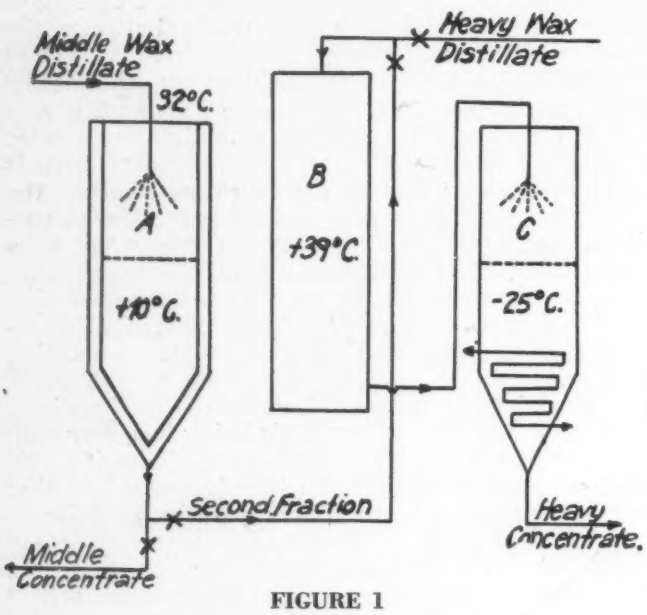

FIGURE 1

coolers from distillate tanks, where the temperature should be 2 to 3° C higher than the melting point of the wax distillate. The cooled distillate of the first fraction shows wax particles crystallized in needles which grow in longer and thicker needles with lowering of temperature. The reason of this phenomenon is that the lower-melting wax particles are successively adsorbed on the surface of the higher-melting needles.

The oil filters through the press rapidly, leaving behind a slack wax of needle crystals. The more needles the wax distillate contains the higher the content of wax in the slack wax. In other words, the amount of oil in slack wax is due primarily to the crystalline nature of the wax. The single-pressed slack wax contains a structure of needle crystals which, when cooling in the sweating chamber, forms a skeleton through which the oil flows easily. Considering the characteristics of the wax distillate cut 0.845-0.870/15, we are forced to the conclusion that this fraction must be submitted to dewaxing separately. But the second and third fractions differ entirely from the first.

The writer has studied this problem and has come to certain conclusions. It has been found that when a warmed wax distillate with wax plates is brought into contact suddenly with cold water, the wax plates solidify instantly into needle crystals, thus causing a separation of the needle structure from the mother liquor. The warmer the wax distillate and the colder the water the longer and thicker are the needle crystals. Of course, there are temperature limits which must not be exceeded, and these have to be determined for each distillate. This phenomenon caused the author to develop a new type of chilling machine. This is a fractionation chiller, shown in Figure 1, which consists of a vertical cylinder equipped in its middle with a sieve. The outside surface of the column is cooled with water.

When the wax distillate particles fall on the surface of the cold water, a splitting up into needle crystals and the mother liquor occurs because of the great difference of melting points. In other words, the low temperature reduces the surface tension of the wax particles, causing their growth into needle crystals. When processing the distillate with wax plates in the fractionating cooler, separation into two fractions occurs. The first upper fraction has a highly concentrated wax structure with well developed needles, and therefore may be easily sweated. The second contains the wax particles as plates, and thus cannot be easily sweated. It must, therefore, be recrystallized.

This process can be carried out in the same fractionating cooler. When the operation is completed, the water is drawn off, and then the oil containing the paraffin plates. The paraffin-wax concentrate remains in the cooler as a solid mass, and must be melted to make it possible to pump. This wax distillate shows all the characteristics of a slack wax of high quality, and therefore it may be submitted to a sweating process. In that event this process shows quite other results. As already mentioned, in carrying out the sweating process two cuts are obtained, their yields depending upon the character of the paraffin-wax structure. The separation between the needles and the oil takes place during cooling in the sweating chamber. The oil lies freely between the needles, and when the material for sweating is warmed the oil flows down through the skeleton of the needle structure, forming paraffin wax free of oil.

By thoroughly sweating the paraffin-wax concentrate formed by means of these methods (that is, by using a proper temperature and time), a sweating oil can be obtained with a solid point below 0° C. However, this process also has some disadvantages. The second fraction obtained in the cooler contains paraffin wax particles in the form of plates. It must, therefore, be submitted to a recrystallization in the same fractionating chiller.

The reason for this is that a great quantity of wax-crystallizing inhibitor exists in an oversaturated state. Microscopic investigation of this fraction has established that the plates are considerably less than those of the primary material. In other words, the higher concentration of the inhibitors in this fraction forms an intermediate structure between the plates and the amorphous particles. It would be necessary therefore to treat this fraction together with the third heavy fraction obtained between 0.895-0.940/15° C.

As already mentioned, this fraction contains two films of a tarry or resin-like substance that prevent the growth of crystals. These characteristics do not permit it to be pressed and sweated. To improve the quality of this heavy wax-distillate, concentrated sul-

furic acid is used. This destroys hydrocarbons of tar and resin-like nature, leading to better crystallization. But it was found by microscopic investigations that this process canot transform all wax particles into needle crystals, the rest having the structure of plates. In the writer's opinion, a wax particle in a heavy wax distillate is surrounded by two protective films, the first consisting of hydrocarbons of tar and resin-like nature, the second and interior film containing certain oily higher molecular hydrocarbons of unknown nature.

When diluting this heavy wax distillate with gasoline, or treating it with sulfuric acid, only the first exterior protective film is split up. But the surface tension of the wax particles cannot disappear completely because the second film produces a certain surface tension. Therefore the amorphous structure of the wax particles can be transformed into plates, when using these methods. To transform the amorphous wax particles into needle crystals, that is, to reduce the entire surface on such a particle, the writer has used the same apparatus as that mentioned, but instead of cold water used a mixture of 95 percent benzol and 5 percent phenol. The fractionating chiller is filled with the mixture of benzol and phenol to the level of the sieve. The part between the sieve and the bottom is equipped with a coil through which chlor-magnesium solution flows continually from the compressor. The warmed heavy wax distillate is pumped into the top of this crystallizator.

The distillate falls as a spray upon the surface of the sieve. Sudden cooling of the wax distillate causes a great difference of heat conduction between the wax particles and the two surrounded films. This leads to their splitting off from the surface of the wax particles. This is the reason of the transformation of plates into needle crystals. Of course, phenol plays the role of a proper solvent that is able to make a complex compound with inhibitors and facilitates the development of needle crystals.

This process results in the following two fractions: The first upper fraction showing a highly concentrated paraffin-wax structure with the developed needle crystals; and the second being nothing more than a solution of the oil in the solvent. After the operation is completed the solution is drawn off, and the paraffin-wax concentrate, being in a solid state, must be melted to make it pumpable. The heavy wax concentrate thus obtained now can be submitted to the sweating process with excellent results. Considering the run of the middle and heavy wax distillate, it will be seen that two coolers are necessary in carrying out this process. Figure 1 shows the flow of this process.

This procedure of crystallization and filtration without filter presses differs from the conventional method by which primary and secondary recrystallized slack waxes are obtained, and the fractionating chiller presents a greatly simplified method of dewaxing by which an increasing of paraffin wax yield can be obtained.

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[2] Petr. Zeitsch. 1923, p. 183.
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TESTING GREASES

(*Continued from page 470*)

siderably and led them to suggest a classification of lubricating greases on that basis. The tough, long fibre grease being at one end and the smooth, short fibre at the other end of the scale. This method should prove useful for special greases and in development work but due to time and extreme care required will probably not be adapted to routine control.

C. L. Knopf[5] has developed ingenious apparatus and methods for determining consistency and other physical characteristics of lubricating greases. Some of them are best adapted for use in a cold room or a cabinet with temperature control which usually are not available in smaller laboratories and might restrict their general use. Others could be readily used by even the smallest grease manufacturer and found helpful for control.

Just a few words on machines for testing extreme pressure properties of gear lubricants. The S.A.E. machine developed by cooperation of manufacturers of gears, bearings, lubricants and automobiles together with the Bureau of Standards, Society of Automotive Engineers and other technical societies has had increasing use. Under guidance of the S.A.E. twenty-one of the machines were manufactured and delivered in 1935, 10 more were made and put in use in 1936 and an additional 10 machines are now being manufactured. A standard method of procedure has been prepared by a committee and is in use by operators. The machine has been found useful in predicting performance of extreme pressure lubricants as to load carrying in service, but up to the present time results obtained in the various laboratories have not checked as closely as desired. There is no way now to determine wear on the S.A.E. machine.

The Timken lubricant tester has been revised especially as to application of load and a new method of procedure worked out which gives much promise for accurate results. It is being used for laboratory control of extreme pressure lubricants by several companies and results from individual laboratories on the same products have been exceedingly close together. Wear can readily be determined as well as E.P. properties.

The Falex machine (formerly Cornell machine) has been widely used for sales purposes. With it both load carrying and wear can be checked in a comparatively short time. There is the advantage that the machine is small enough so that it may be readily transported. Changes in the machine and operation have been made in the last year which should improve its value.

There is general accord that a machine is badly needed which will really give a complete picture in the laboratory as to what may be expected of the lubricant on the road. That is not possible at present but the fine work which is being done will no doubt result in reaching such a goal.

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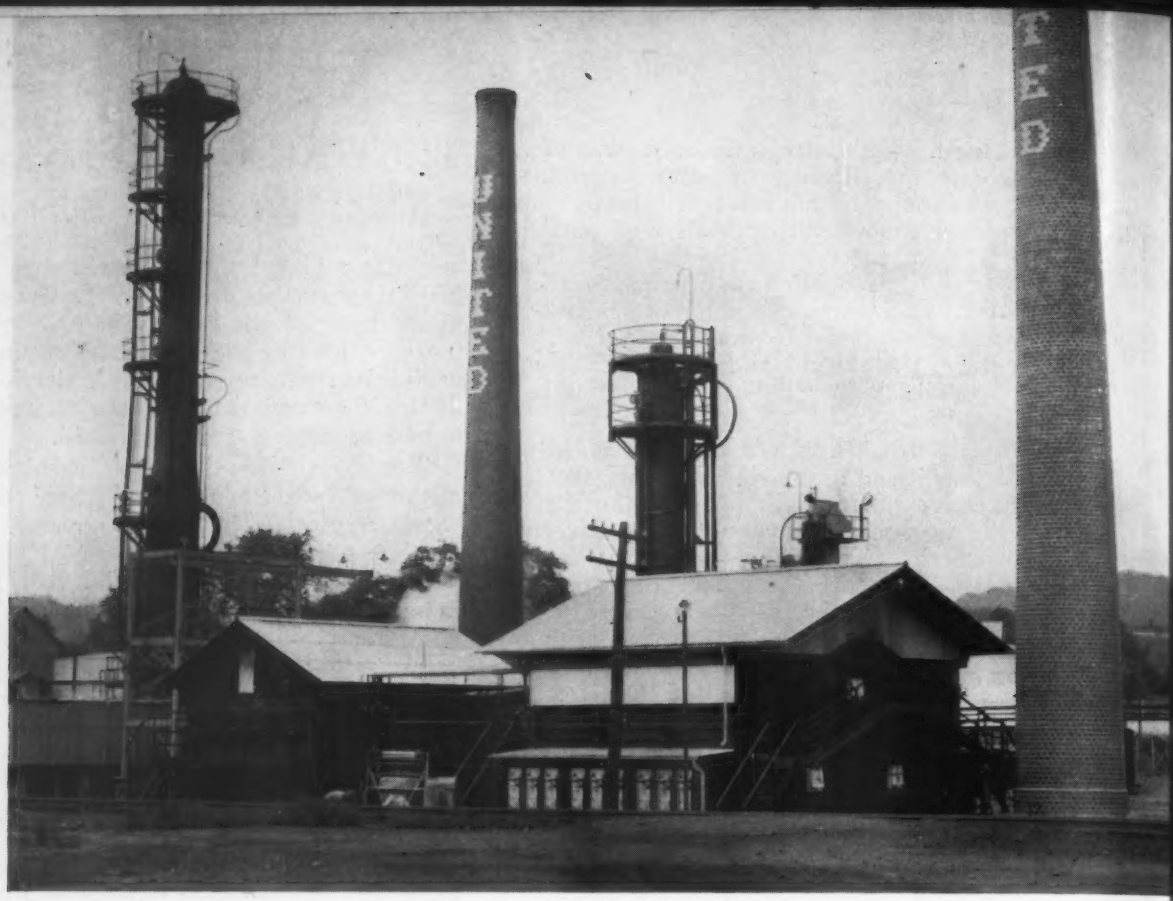


Dubbs unit completed in 1936 to handle petrolatum, fuel oil and naphthas for high-octane gasoline production.

Modern Distillation And Cracking Operations

At United's Warren Refinery

J. C. ALBRIGHT

BY CARRYING on a steady expansion program which has extended over several years, United Refining Company, Warren, Pennsylvania, has brought its refinery up-to-date. During depression years, when the average refiner was operating under difficulty this company continued to improve its facilities and enlarged its plant and installed modern machinery in the wax and lubricating oil division, which included the wax plant, the filter plants, centrifuge room and crude unit. The crude unit was erected 2 years ago, and is designed by engineers with the United Refining Company and Arthur G. McKee & Company. It was built to produce, almost at a moments notice, practically any grade of products which can be manufactured from Bradford crude oil.

The first process through which the crude is put is a combination of salt-removing vessel and dehydrating unit. The vessel, which is a horizontal unit, has sufficient capacity that the crude takes about four hours to pass from one end to the other at about 180° F. Baffles in the vessel changes the flow of the oil abruptly numerous times, causing the water and foreign matter to be precipitated. During the preliminary process of cleaning up the oil, a short cut of gasoline is removed, passed through a short bubble tower on top of the vessel for fractionation, and condensed in separate units. Distillation of the lighter fractions is more or less incidental to the primary processing, and advantage is taken of the heat to relieve the main column of such gas load when the oil is passed through the main unit.

The principal object in processing the crude through the primary equipment is to clean it so that no foreign matter will be contained in the cylinder stocks. The exclusion of any matter, other than clean petroleum, lightens the load on subsequent operations, and also prevents contamination of baffles and

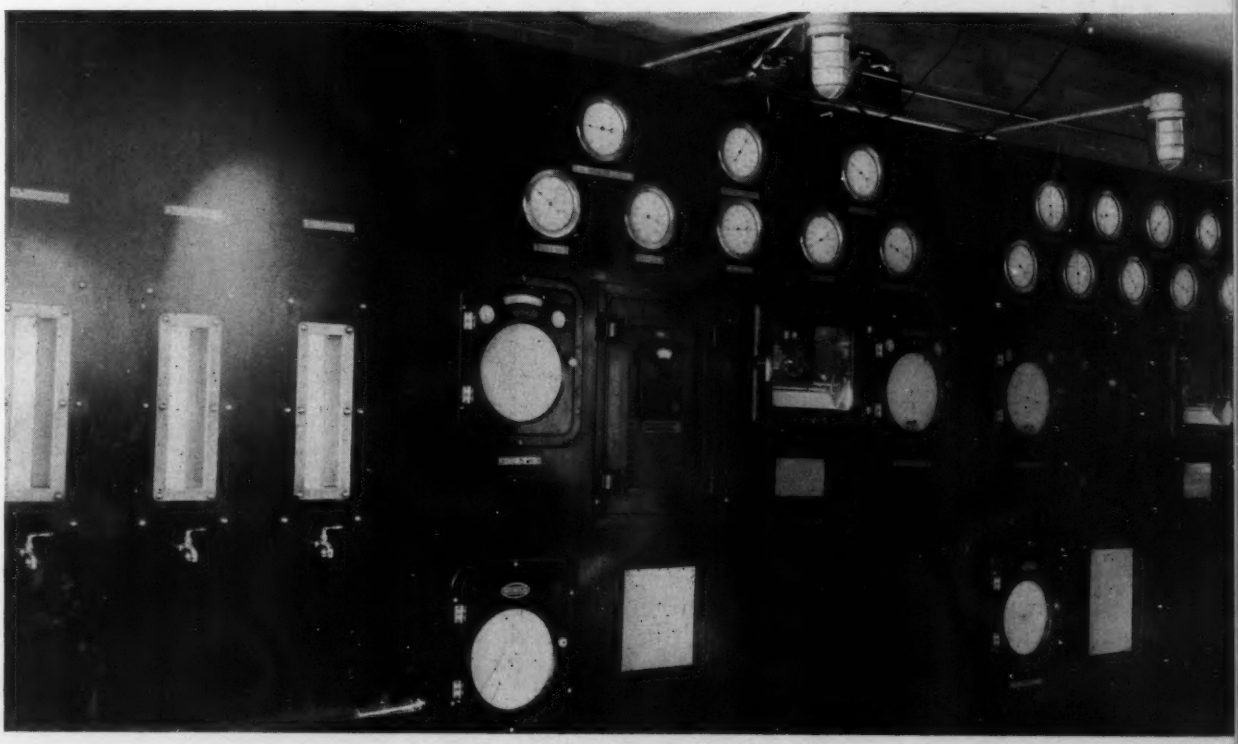
bubble trays in the main fractionating column. The term "salt settler" is somewhat of a misnomer when applied to the horizontal vessel, as very little salt is produced with the oil, and as a consequence, chloride corrosion is practically absent in this plant. Comparatively little pressure is applied to the primary process. Two pumps are used before the oil enters the furnace. The second pump takes suction on the outlet of the settling tank, and forces the clean charge through adequate exchangers to the inlet of the tube heater. The heat picked up by the crude before it enters the furnace is supplied by the bottoms and two side cuts from the tower. Heat supplied to enable the sediment and impurities to settle in the four hour travel through the horizontal primary process is obtained by overhead vapors-to-crude charge—three shell and tube units above the gasoline condensers being used for this purpose.

The temperature of the material passing through the furnace tubes varies from product to product, as sales requirements vary, so no cut-and-dried program is followed in operating the furnace and fractionating column. The furnace itself was designed to contain roof and wall radiant and a convection bank of tubes, which has recently been redesigned to contain a set of floor tubes. After applying the proper degree of heat to the clean oil in the furnace tubes, it is transferred to the side of the fractionating tower through a tangential nozzle, for added turbulence, and is fractionated into seven different streams in addition to the bottoms. Straight-run gasoline is removed from the overhead section, using two vapor lines to lead the gases from the tower to the crude-to-charge exchangers. Internal stripper sections provide efficient fractionating facilities so definite cuts can be removed as finished products, exclusive of treating.

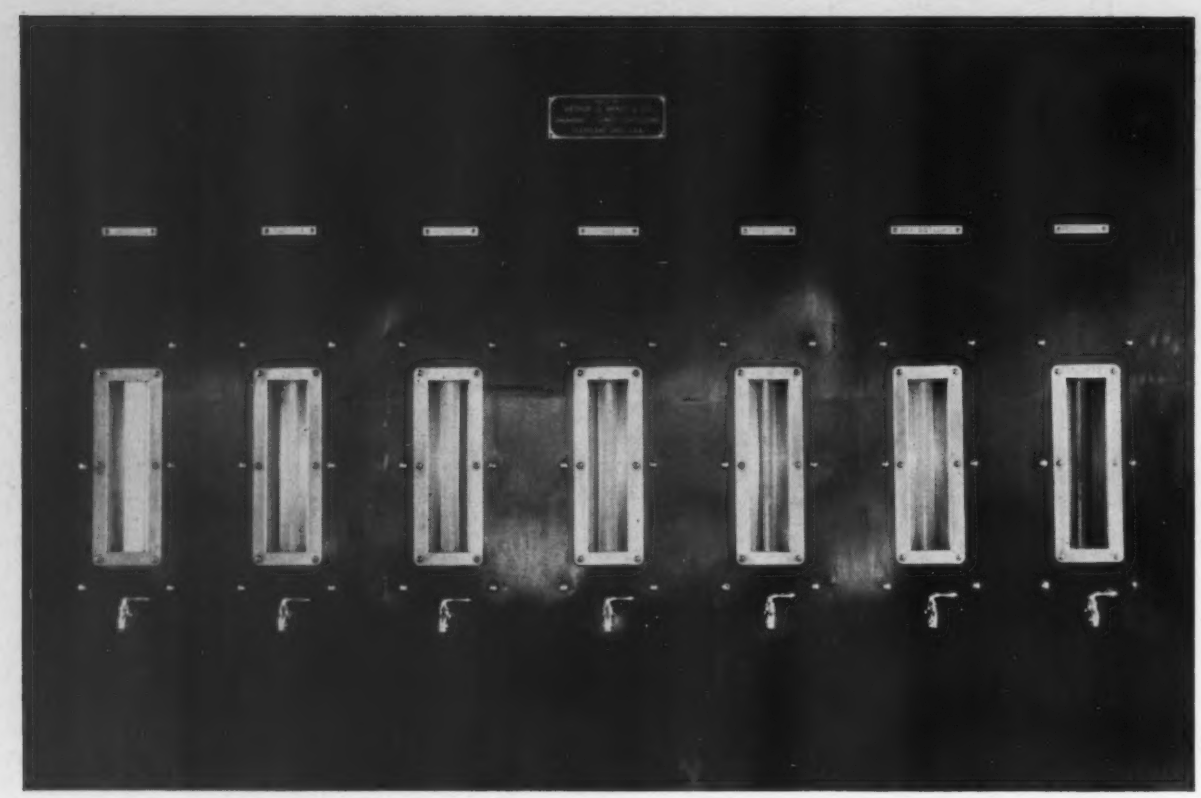
INSTRUMENT CONTROL

The column, 120 feet high over-all, is equipped with a circular stairway for convenience to the operators when it becomes necessary to make adjustments on outlet connections and other equipment. The spacing of the landings between stair sections is made so that bolted man-ways can be inspected without straining upward, or stooping unduly. Many instruments are attached to various points in this system so adequate and definite control may be obtained, with the instruments installed both in the control room and near the base of the column and around the unit. The recording and indicating potentiometers are installed on the board in the control room where it is convenient for the operators to observe the operation of the plant. The indicating potentiometer has a large number of points, among which are those connected to the following places: settling tank, still outlet and inlet, still bridge wall, still flue gasses, inlet and outlet of floor tubes, inlet and outlet of roof tubes, overhead outlet of vapors, naphtha stream take-off, kerosene section, furnace oil stream, fuel oil stream, slop-wax cut, wax distillate stream, vaporizer section, bottoms, side-to-side and bottom strippers and eight trays in the column where the various fractions are being separated and produced from the crude charge. The recording potentiometer writes a permanent record of temperatures on the inlet and outlet of the pipe still, temperatures maintained on the top of the tower and the vaporizer section temperature.

Automatic temperature and flow controllers are also located on the control panel which take care of the charge to the settling tank and from the tank to the still, two units being used for this purpose, one on the cold crude pump and another on the hot charge pump. These two instruments are adjustable to syn-



Control board of the crude unit centralizes information on operating conditions in all parts of the plant.



Seven streams on the indicator board show that many products being manufactured at the same time.

chronize the speed of the pumps so a constant flow is being made to the settler, and a constant relative withdrawal is maintained. All other points in the system which are essential to the flexible operation of the plant are controlled by recording-controllers, any of which may be adjusted for immediate change in operation so a different product may be obtained at a moments notice. The principal changes in the operation of the tower effects the bottoms particularly, with follow-up changes effecting the entire tower as well. Gasoline overhead, naphtha, kerosene, furnace and fuel oil streams are kept at constant composition and specifications, so different ratios of reflux must be applied to these sections when changes in the system vary over a few degrees. The "slack" in the temperature is taken up, after definite bottoms are produced, by the slop wax and wax distillate streams. For example when more heat is applied to the furnace, which reflects on the transfer line to obtain a higher flash-and-fire bottom cylinder stock, a greater amount of the more volatile fractions are driven from the charge, which reflect all the way to the top of the column. By trimming the various sections of the tower, the specifications of the various products are maintained, but allowing the two cuts next to the base to change in composition. Conversely, when a lighter fire is maintained in the furnace, less of the heavier volatile products are driven from the crude, and less trimming is essential to produce the desired definite products. Again the slop wax and wax distillate "take up the slack" by varying in composition to balance the streams removed above and below their accumulator sections.

If at any time during the change in temperature conditions, a side or overhead cut comes off specification, manual controls in the room containing the instrument board can be operated to divert the stream from the run-down line back to the tower for reprocessing until that section becomes normal. A look box, consisting of cylindrical glass tubes inserted in the stream lines, is installed so visual control may be obtained at the time samples are taken. The usual procedure is followed which takes care of only a portion of the stream through the glass tubes, with part of the material flowing through a by-pass arrangement to the run-down tank. However, a sufficient amount of each product is kept flowing through these tubes so relative colors may be observed. By using this installation, no product having specifications other than that desired is ever run to storage, which makes it possible to produce any grade of petroleum product within the capacity of the unit and the character of the crude oil being charged.

RERUN BATTERY

A secondary unit built beside the main distillation unit is essential to the complete operation of the plant as a whole, and consists of a rerun battery, made up of a tube still and fractionating tower. The material normally pumped to this unit is pressed distillate, and the products derived from this charge vary as to the heat and tower trim. Four different streams are removed from the tower, which include overhead gas-oil, a No. 1 neutral side stream, a No. 2 side stream and viscous neutral bottoms. The charge is taken from storage and pumped through gas-oil vapor exchangers and thence to the tube still where definite temperatures are applied to obtain the required products. Overhead control is by reflux, with gas-oil being returned to the top of the column to maintain a constant temperature. The overhead and two side streams are piped to the control room and flow through cylindrical look box tubes similar to those on the main unit. The same arrangement is followed when any cut is off specification and is returned to the column by diverting the flow so no

product is run to storage other than that desired.

As in most other instances in Pennsylvania, refineries were built beside streams available for barging products, and this plant was originally laid out some 35 years ago on the north bank of the Allegheny river. The plant occupies a long, narrow strip of ground between the Pennsylvania tracks and the residence section of the city. Subsequent planning was followed that permitted the plant production to flow in two separate directions; the light oils piped up river and the bottoms down towards the filter house and refrigeration plant. Piping in the yard is carried in concrete-lined trenches covered with fabricated steel grating. Despite severe winter weather in this section, it is said that trenches serve better, as a whole, than covered lines. Lines carrying water and petroleum products are widely spaced and supported on spacers which prevent contact with the floor of the trenches except at the point of support. Water and waste flows along the floor of the trench to a catch-basin, which is processed by adequate skimming to recover any oil leaking from connections or accidentally spilled. All light oil products are practically dry of moisture when they leave the accumulator drums, and it is said relatively few freeze-ups have been encountered.

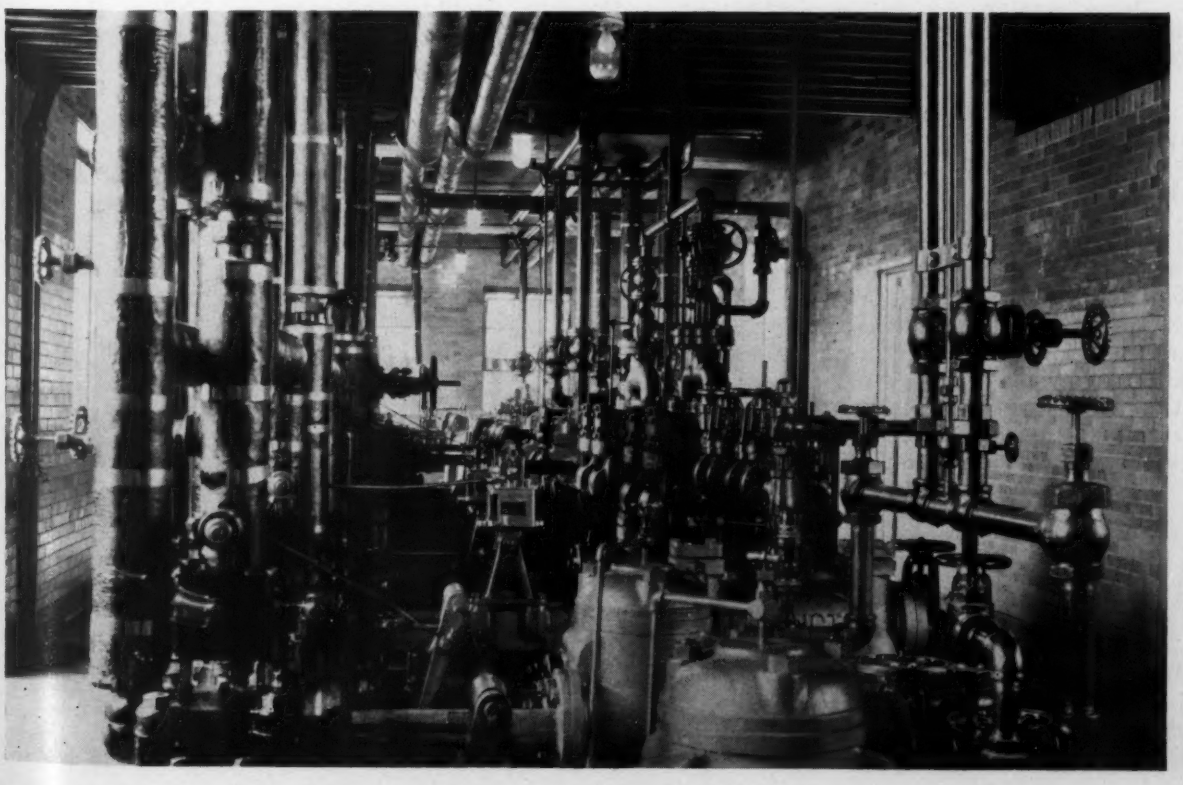
The plant run-down and stock tanks placed in an orderly manner in the yard are all equipped with overhead walks, which connect at all points for convenience in gauging or sampling. Particular attention is given the safety of the employe and walks within the plant, which are elevated, are equipped with hand rails and floors with grating. The stairways around the main and secondary columns are built so a minimum amount of effort need be expended in climbing, and no pit-falls are evident that might be instrumental in causing injuries to workmen in the yard.

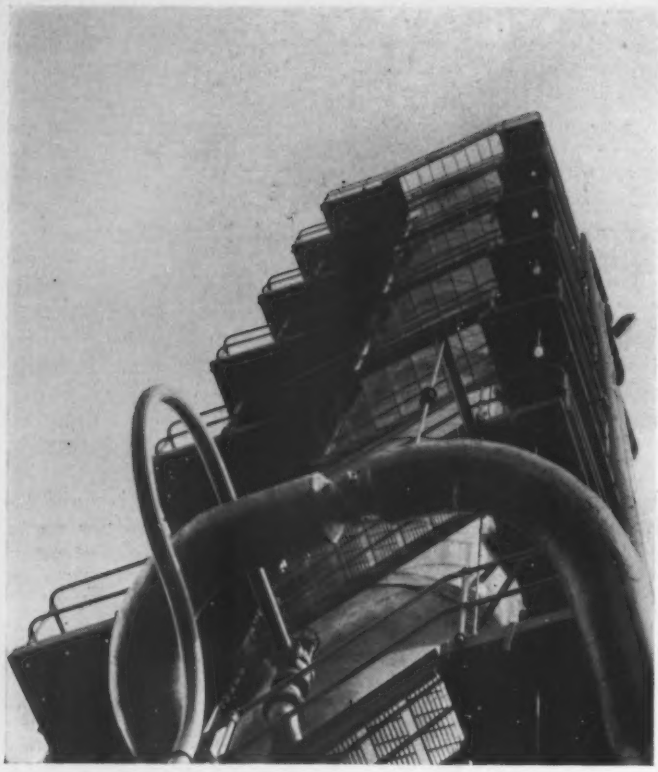
Since this combination crude and rerun unit, which is in reality two plants, was rebuilt by installing floor tubes in the main furnace early in 1937, the cracking plant was redesigned for two-coil selective cracking of various products manufactured in the plant, and purchased outside. Higher-octane gasoline being required for adequate distribution of this product made it necessary to produce a greater amount to compensate for the lower-octane straight-run gasoline made in the crude unit. During the past year it became evident that a larger supply of power and process steam was needed, which brought about the erection of a modern boiler plant, which is equipped to utilize three fuels at will; pulverized slack coal, fuel oil from the bottoms at the cracking unit and gas from the accumulator drums and stabilizers in the refinery. This unit is one of the first to be built which can be fired with pulverized coal utilizing natural draft in the combustion chambers. Smaller units have been built along similar lines, but this unit was designed for an output of 1,160 horsepower. The operation of the refinery as a whole is said to have been greatly improved since these boilers were placed on the line, and therefore a much greater throughput can be processed, due to continuous operation without interruption in power.

Water for plant use is obtained from three separate sources. When the original plant was built, the only supply available was from the river, but during the past year, two other sources have been developed, one at the boiler house, lifted by a steam turbine-driven deep well pump and from other wells within the plant yard. No shortage of water can now shut the plant down.

Straight-run cracked gasolines are treated by the doctor method, using a continuous unit, and after treatment and stabilizing the cracked product, blending is accomplished to produce the required specification motor fuel for the territory in which it is sold. All processes are followed in this refinery to produce the greatest number of marketable products, except greases, that can be manufactured with economy.

Pumps for the crude unit.





Tower ladders are guarded by steel gratings.

White scale wax, cylinder stocks and neutrals are manufactured and sold as separate products, as well as the company's branded line of finished motor oils.

It has been the practice of the management of United Refining Company to shut down each unit periodically for inspection and cleaning, rather than to set running time as a goal, so that all equipment may be kept in first class working order. Pumps are as bright and well cared for after years of operation as when new, and one must look a second time to determine which is old and which is new. Leaks are repaired at the time they show, and rust is prevented by a well-planned painting program that keeps all tankage, pumping equipment and other units in spick-and-span condition. And as one of the operators put it, it is much easier to operate a well-kept, good-looking plant than one which is allowed to run down at the heels.

CRACKING OPERATIONS

Early in 1936, this company, following the expansion and rebuilding of the distillation unit, built a cracking unit to take care of approximately 1000 barrels of charging stock per day. Various materials were available for cracking, as well as some of the lighter naphthas were available for reforming.

Following the plan of keeping the light oil part of the plant as far removed from the refrigeration and lubricating oil preparation, the cracking unit was erected on the extreme up-river end of the properties. Two furnaces are included in the design of this plant; one especially for fuel oil cracking and reforming, and the other to handle any other products that might be available. The heavy oil furnace is operated as a heavy oil cracking unit when sufficient stocks have been accumulated to justify a run. After this material has been consumed, the unit is usually shut down, cleaned out and inspected, after which it is again fired up and operated with about a 50 gravity distillate as a reforming stock. When conditions are such that both furnaces may be operated, the smaller of the two is charged with distillate while the heavy oil furnace is being charged with fuel oil.

On a recent run, handling a 39.6° A. P. I. charging stock, which contained about 9.8 percent petrolatum, 43,443.43 barrels were pumped to the unit, averaging 1010.3 barrels per day, with a recycle of 976.3 barrels per day. The operation was full flashing, and the tabulation of the run is as follows:

CHARGE

Raw oil charged	1010.3 bbls. per day
Recycle	976.3 bbls. per day

PRODUCTION

End point distillate	792.4 bbls. per day
Residuum fuel oil	135.3 bbls. per day
Coke, gas and loss	82.6 bbls. per day

TOTAL PERIOD

Raw oil charged	43,443.43 barrels
End point distillate,	34,074.25 barrels
Residuum fuel oil	5,819.71 barrels
Coke, gas and loss	3,549.47 barrels
Gas production	15,839,100 cu. ft.
Gas production	364.35 cu. ft./bbl. charged

FUEL CONSUMPTION

Oil-resid-fuel oil	3,414.39 bbls.
Gas	3,719,800.00 cu. ft.
Total fuel burned	10 percent of raw oil charged

The analysis, ASTM, of raw charge is as follows:

STOCK

Gravity, °'s A.P.I.	39.6
I. B. P.	248° F.
10%	487° F.
20	546° F.
30	560° F.
40	571° F.
50	582° F.
60	593° F.
70	604° F.
80	619° F.
90	640° F.
E. P.	675° F.

Pressure distillate, end point production. The production analysis is as follows, gasoline produced:

Gravity	62.0° A.P.I.
I. B. P.	82° F.
50%	275° F.
E. P.	410° F.
R. V. P.	9.5 pounds
Antiknock value, Octane number	66.5

The average operating conditions while this run was being made are as follows:

TEMPERATURES

Furnace, heating	1215° F.
Furnace, heating	1215° F.
Furnace, soaking	1290° F.
Furnace, soaking	1290° F.
Combined feed-at Furnace	620° F.
Transfer line	925° F.
Flash chamber inlet	740° F.
Resid. draw-off	680° F.
Vapors to fractionating tower	725° F.
Top of fractionating tower	370° F.
Bottom of fractionating tower	625° F.

PRESSURES

Hot oil pump discharge	600 Pounds
Reaction chamber	445 Pounds
Flash chamber	60 Pounds
E. P. distillate receiver	45 Pounds

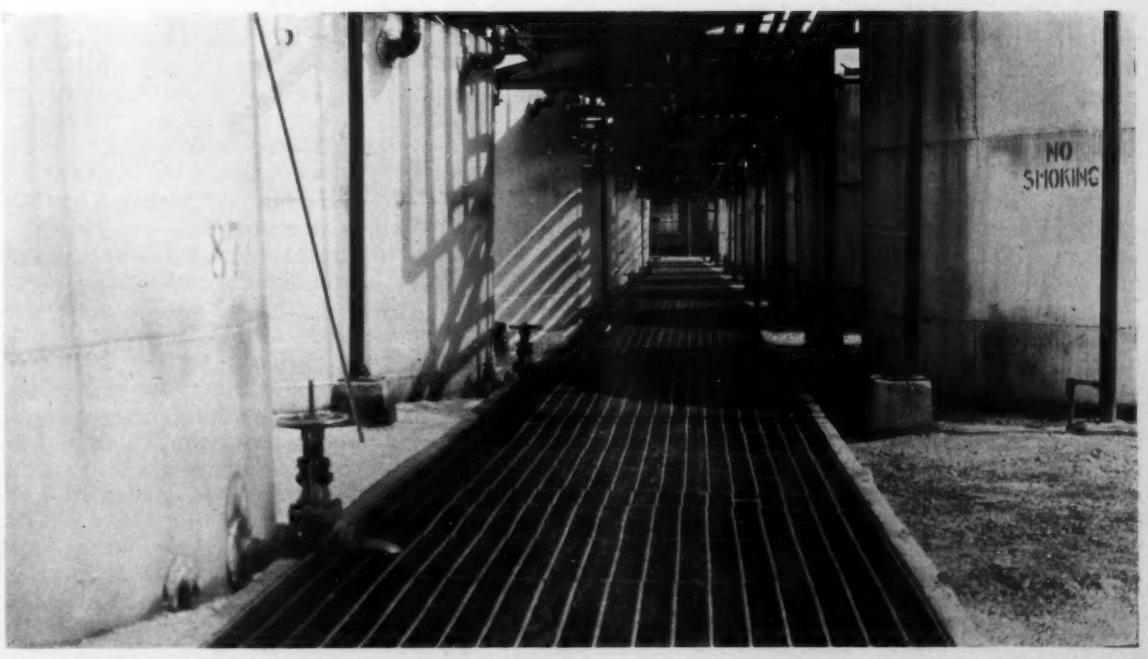
In this operation, the raw oil is picked up by an

Safety walks protect workers on run-down tanks.

outside packed plunger pump driven by a horizontal, single cylinder 12 x 12 steam engine at the supply tank and forced through exchangers, after passing through the absorber, to the furnace. This furnace is a double end-fired unit with floor tubes. The transfer of the oil is directly to the reaction chamber, which has a pressure-regulating slide valve and out to the combination flash and fractionating tower. Gasoline vapors, remaining in the residue gas from the pressure distillate stabilizer, are passed with the raw charge through the cracking operation and follow through to the condensers with the gasoline produced by cracking.

Residuum fuel oil is used as fuel on one side of the double furnace, while cracked gases are burned in the duplicate end of the unit. Either residuum fuel oil or gas may be used at will, depending upon the availability of the fuels in the plant. A large amount of the gas produced is used in the crude unit in the refinery, which must operate at predetermined temperatures for efficient manufacture of the products desired. Some gas is used in the steam generating units, especially to keep one of the units almost at steaming temperature for instant use, should steam be needed in excess of that produced normally.

The top of the fractionating column is maintained at the desired temperature so end point pressure distillate may be produced without subsequent processing. The vapors are carried through coolers and to the pressure distillate accumulator where they are pumped to the stabilizer for extracting butanes to lower the vapor pressure to that required at various periods of the year. The cooled, stabilized distillate is then run to storage, from which it is later pumped to blending tanks where straight-run gasoline is used, and treated in a continuous doctor plant for sweetening.



Steel grating covers the pipe trench.

Practical Methods of Preventing Corrosion *From Mid-Continent Crude*

ROBERT E. PUCKETT*
Barnsdall Refining Corporation

WITHIN recent years the Kansas refiner has been brought face to face with the problem of handling a crude charge which is far more corrosive than any oil he has experienced in the past. At least in a few instances the corrosive action of the crude oil was so severe that the problem had to be solved immediately or operations suspended. Unfortunately, the refiner was given no warning of an impending run of severely corrosive charging stock. Frequently it was not discovered that the crude oil had gone suddenly corrosive until after costly damage had been done. Invariably the plant laboratory staff was called upon to suggest a remedy and to do so immediately. Under such conditions the chemist was forced to take a pot shot at the problem without the benefit of a scientific investigation which if made at all was more in the nature of a post mortem.

In the Wichita plant of Barnsdall Refining Corporation no serious corrosive troubles were experienced until October, 1935. Two pipe stills and four Dubbs cracking units had been running for approximately 8 years without any indication of unusual deterioration of equipment.

Within a period of 60 days the pipe still began leaking around the rivets in the bubble tower—some tray decks were nearly destroyed. Bubble caps became clogged. The water from the draw-off separator in the lines to the tanks was saturated with iron salts. The indications were that the bubble tower would not last another three months. Immediately following these signs of disintegration, the cracking plant began losing tubes with unusual frequency. Corrosion within the reaction chambers speeded up at an alarming rate. The situation demanded a quick solution to the problem.

The principal chemical characteristic was an acid crude charge having a salt content of 55 pounds of sodium chloride, 6 pounds of magnesium chloride and 26 pounds of calcium chloride per 1000 barrels. Water taken from the separator on the sour gasoline line was saturated with iron chloride. Evaporation of the water gave a heavy precipitate of the iron salt.

Ammonia gas was introduced into the fractionating tower at the kerosine pan. This arrangement did not appear to be giving all the results desired. Ammonia was then injected into the cold crude-oil charging pump. Injection of ammonia at this point was contrary to the recommendations of the manufacturers who state that the gas is decomposed at around 800°F. Following the injection of ammonia into the crude charging pump an immediate improvement was noticed on the crude still. The draw-off water ceased running a stream of dissolved iron. The fractionating tower which had undergone recent repairs showed no further leaks or evidence of corrosion. Leaks in the crude oil heat exchanger became noticeably infrequent. The same result was experienced on the furnace tubes. An unexpected result took place by feeding the ammonia directly through the crude furnaces. Ammonia compounds of high boiling range were formed which gave an alkaline characteristic to the topped crude.

When this fuel was rerun in the Dubbs cracking still the ammonia compounds afforded almost complete corrosion prevention. The cracked pressure distillate was definitely alkaline. Even the coke from these units was alkaline. Replacement of tubes in the Dubbs plant dropped about 75 percent. To accomplish these results required about 8 pounds of ammonia per 1000 barrels charged through the crude stills. The gas was controlled by the standard manometer type flow control. In order that uniform ammonia pressure be maintained the tanks were immersed in a water bath.

The results achieved with ammonia injected into the crude furnace can be duplicated where similar circumstances prevail. In the crude furnace the maximum temperature was not over 750°F. The tubes were carbon steel, 3½-inch I.D. and 4-inch O.D. The pressure within the tubes was only a few pounds over atmospheric. The velocity of flow was 3½ feet per second. The refractionating tower was constructed of riveted ½-inch steel plate with a maximum of 750°F. temperature at the base and 320°F. at the top. The internal pressure was atmospheric. The condenser was cast iron and made with the conventional radiating fins.

A heat exchanger with a counterflow of hot fuel oil and cold crude had become a constant source of trouble due to corroded tubes and consequent leaks. With ammonia saturating the incoming crude oil and the hot residual fuel as well, satisfactory protection was given this important part of the refining equipment. Owing to the fact the heat-exchanger tubes were steel, we could maintain this alkaline condition without danger of damage from the alkali itself. The cracking unit, which rather unexpectedly received the benefits of ammonia injection, was using carbon steel tubes 3½ inches I.D. and 4 inches O.D. Pressure within the tubes was 200 pounds per square inch with a maximum temperature of 900°F.

Under working conditions of the same order as described reasonable protection is given by ammonia for the prevention of corrosion. We must further

*Presented before the Regional Meeting of the Western Petroleum Refiners Association at Wichita, Kansas, September 21, 1937.

qualify these results by a study of the type of corrosion which the ammonia minimized. In general, corrosion causes fall into two divisions: low-temperature or electrolytic (below the boiling point of water) and high-temperature corrosion by direct chemical action. Within the heat exchanger, furnace, and tower of the crude still the corrosion was due to direct chemical action. According to the work of Wood, Sheely, and Trusty (Ind. & Eng. Chem. 17) 798 (1925) the following sulfur compounds are reported as active corroding agents. (Test conducted at room temperature.)

A. Mercaptan sulfur is most corrosive, forming mercaptides of iron and copper.
B. Hydrogen sulfide is very reactive, forming iron and copper sulfide.
C. Free sulfur is quite inactive with iron but corrodes copper and brass.
D. Other sulfur compounds are only slightly corrosive.
E. In all cases corrosion is accelerated by the presence of water.

Later work by Retailliau and Lang, Proc. A.P.I. 10, 158 (1929) records elementary sulfur as the most corrosive agent likely to be encountered at temperature around 900°F. Wilson and Bahlke (Ind. & Eng. Chem. 17, 355 (1925) believe sulfur and hydrogen sulfide to be quite active at temperatures around 700°F., and almost without action at 500°F. and below. Laboratory records did not indicate any change in sulfur content following the suddenly developed corrosion problem in our refinery. Sulfur or hydrogen sulfide corrosion without question was taking place within the still but to a negligible degree as the equipment had operated trouble-free for approximately 8 years under similar conditions. Evidence at hand automatically rules out sulfur or its compounds as the sole cause of this especially reactive period.

A close inspection of the crude oil was made. Taking into account a number of analyses the crude oil contained the following adulterants: BS&W 1/10 percent total salt as sodium chloride 50 pounds per 1000 barrels, broken down into the actual content: calcium chloride 20 pounds per 1000 barrels, magnesium chloride 6 pounds per 100 barrels, iron chloride 10 pounds per 100 barrels, free hydrochloric acid 3 pounds per 1000 barrels. Hydrogen ion concentration of the crude as determined by contact with an equal volume of distilled water was 3.5 pH.

Magnesium, calcium, and iron chlorides attack iron readily and as they become spent they are continually being regenerated by hydrogen sulfide. A cycle is established which will eventually destroy the equipment. Aside from the acid salts, free hydrochloric acid was present in sufficient quantities to cause considerable damage in itself.

The presence of calcium and magnesium chloride in crude oil was common knowledge and their effect was understood. From the point of view of published information, iron chloride and free hydrochloric acid is an original contribution as its presence evidently was not generally suspected. Later work in our laboratory revealed hydrochloric acid and the pH of crude oil to be factors which could be measured readily. The acidity of crudes from different sources vary as to their free-acid content. We have analysed Kansas crude which ran from a trace to 7 pounds of hydrochloric acid per 1000 barrels.

Judging from published information, the corrosion in our crude-distilling equipment would be caused by sulfur or its compounds in the high-temperature regions and acid and its salts in the condensing section. Contrary to this idea, we believe that hydrochloric acid and acid salts are responsible for the extremely active corrosion we experienced in regions of the still which were as hot as 750° F. This concept may have to be modified when further research work is accomplished. At present we assume that sulfur corrosion had been going on continually at a rate well within reasonable tolerance. To free hydrochloric acid and its salts we have assigned the major responsibility of the unusually active corrosion. Laboratory analyses of the end products of corrosion in the high-temperature sections of the crude still invariably disclosed iron sulfide, iron chloride, free hydrochloric acid, and occasionally calcium and magnesium salts, which further substantiates our opinion that acid corrosion in the high-temperature sections is at least occasionally more destructive than sulfur or its compounds. Many authorities feel that hydrochloric acid corrosion will take place only in low temperature sections, basing their opinion on the fact hydrochloric acid does not dissociate so readily at high temperatures. Free hydrochloric acid must dissociate in order to become an active corrosion factor. Increase in temperature reduces the dissociation but we find the difference in dissociation between temperatures ranging from 65° F. to 700° F. amounts to only a reduction of approximately 30 percent (Electro chemistry. Creighton and Fink, Vol. 1, page 106). There is also a possibility of acid and acid salts setting up an oxidation reduction cell between the still wall and sulfur compounds which pass over the surface.

With sulfur corrosion the end product is iron sulfide which precipitates to form a protective coating. Free dilute hydrochloric acid dissolves this protective coat with the elimination of hydrogen sulfide gas and the formation of iron chloride which is an active electrolyte. Ammonia gas will greatly reduce sulfur corrosion and in addition render still tubes and refractionating towers alkaline. In this condition hydrochloric acid is not permitted to dissolve the natural sulfide protective film.

Ammonia is an extremely valuable asset in the prevention of corrosion in equipment which is operated with low-velocity flow and under low pressure. The only handicap experienced in our refinery has been that under alkaline conditions iron chloride reacts with hydrogen sulfide to deposit iron sulfide in the refractionating tower with consequent stoppage of bubble caps and the small tubes in heat exchangers. This condition is peculiar to crude oils bearing iron salts.

In regard to our particular condition the refractionating tower has been an accumulation point for the end products of a dissolving pipe line which was being attacked by hydrochloric acid. Our observation has been that acid-bearing crude should be neutralized in the field and thereby prevent its contamination by iron salts. Significant with our observation of a suddenly developed corrosive condition in the refinery was the fact that this situation developed shortly after the oil field from which we were pumping had been acidized.

In regard to the use of ammonia for corrosion prevention there is always the question of what degree of alkalinity is necessary for the best control. Some authorities recommend controlling the dosage to where the drawoff water from the condenser traps shows a pH of 6.7 or close to the neutral point. In

view of our experience we believe a pH of 9, which is about the alkalinity required to turn phenolphthalein red, is most desirable. The factor limiting the use of ammonia gas for neutralizing sulfur corrosive compounds is the comparative low heat of formation of the sulfide.

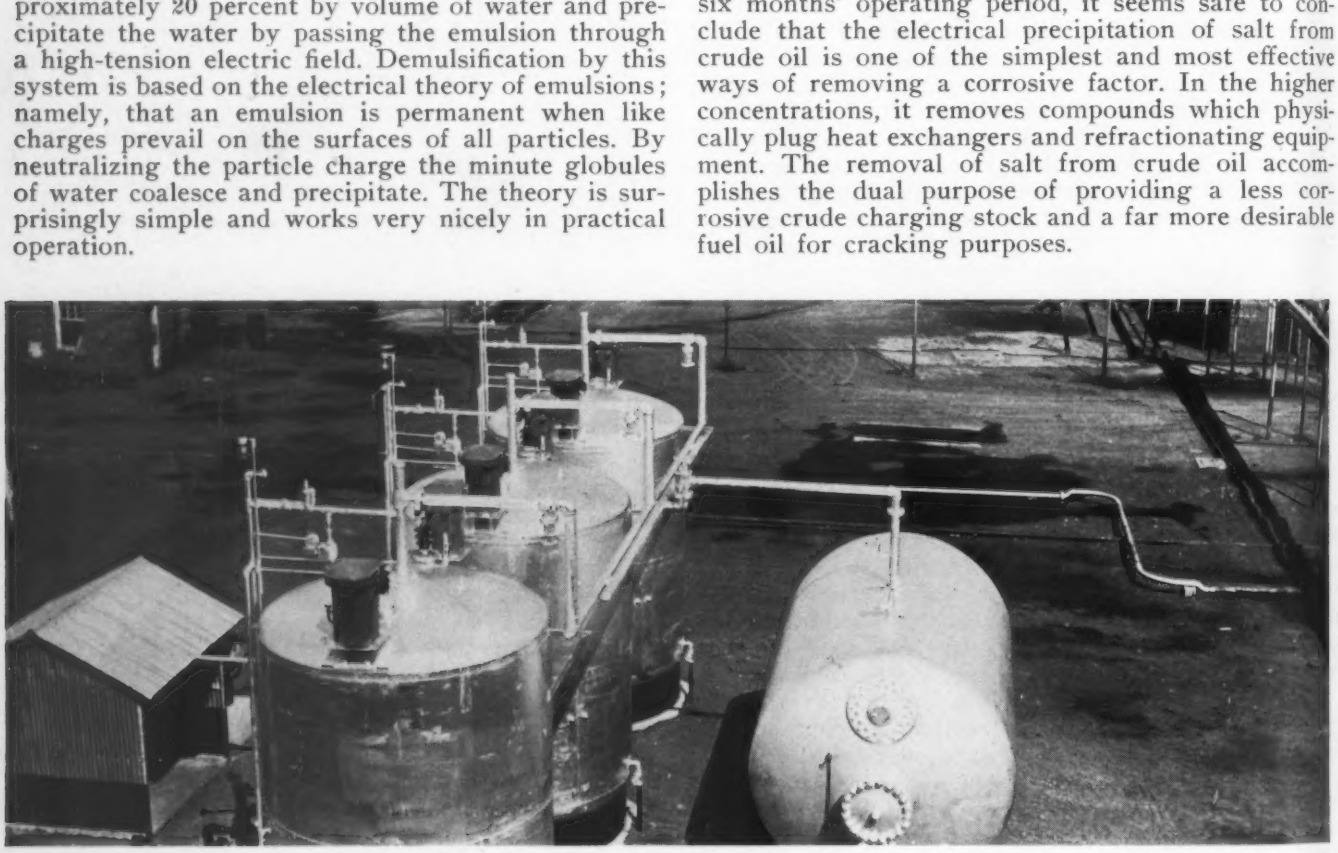
It is our opinion that an excess of ammonia will counteract this weak point by the law of mass action. That is, where ammonium sulfide might decompose and release hydrogen sulfide the mere numerical presence of a number of free ammonia radicals would inhibit the disintegration. Manufacturers of condensers made of copper and zinc alloys recommend that ammonia be fed into the system only to the point of neutralization. However, where the construction materials will permit we believe more complete inhibiting of disintegration is had with a liberal excess of ammonia.

During August, 1936, a system was installed in our refinery to remove salt from the crude oil. The process was, briefly, to scrub the crude oil with approximately 20 percent by volume of water and precipitate the water by passing the emulsion through a high-tension electric field. Demulsification by this system is based on the electrical theory of emulsions; namely, that an emulsion is permanent when like charges prevail on the surfaces of all particles. By neutralizing the particle charge the minute globules of water coalesce and precipitate. The theory is surprisingly simple and works very nicely in practical operation.

reduced in some cases from 6 pounds per 1000 barrels to a mere trace.

An experiment on a 30-pound per 1000 barrels salt content crude oil was made to find the physical form in which the salt was present. This experiment was suggested by the fact the salt content of crude oil is sometimes more concentrated than can be accounted for by assuming the traces of water present as being saturated. In the sample of crude oil in question, half of the corrosive salts were in solution and the other half suspended in the oil as micro particles which cannot be precipitated by centrifugal force. A crude oil of this type could be settled 100 percent free of corrosive salt water yet retain a substantial quantity of corrosive material. The electrical precipitator was capable of scrubbing suspended micro crystals from the oil. The removal of salt in the crystalline form is the most difficult factor to handle, requiring a close grain emulsion scrub for complete removal.

In view of experimental evidence gained from a six months' operating period, it seems safe to conclude that the electrical precipitation of salt from crude oil is one of the simplest and most effective ways of removing a corrosive factor. In the higher concentrations, it removes compounds which physically plug heat exchangers and refractionating equipment. The removal of salt from crude oil accomplishes the dual purpose of providing a less corrosive crude charging stock and a far more desirable fuel oil for cracking purposes.



Electrical desalting process at Barnsdall Refining Corporation's Wichita, Kansas, refinery.

Three full-size commercial precipitators were used in our experimental attempts to desalt crude. Each unit was capable of processing 1500 barrels of crude oil per day. The equipment under correct operating conditions can easily scrub crude oil containing 100 pounds of salt per 1000 barrels, and deliver a pipe line specification crude oil with 5 pounds or less of salt. It is not consistent to estimate the equipment on a percentage basis of salt removal. Our experimental evidence led to the conclusion that if 200-pound salt crude or 10-pound salt crude was charged to the equipment it would consistently deliver a 4- or 5-pound per 1000 barrels product. Besides the removal of corrosive salts, hydrochloric acid was

Prevention of corrosion in distilling equipment appears to be an elusive problem and requires constant vigil to effect complete control. Methods which have been accepted as satisfactory sometimes fail without any obvious reason. Of course, the mysterious shifting of points of most severe corrosion is merely a change in the chemical equations involved; for example: a slight variation of temperature, pressure, moisture content, or velocity of flow will completely change the corrosion picture. The shifting percentage of salt contamination and within the total salts, constant changing of composition also contribute to cause unexpected outbreaks of corrosion. With all of these factors as shifting hazards it is little wonder

that occasionally corrosion slips into the most technically policed refineries.

Following our successful corrosion inhibiting in the crude stills and the cracking units with ammonia, we believed we knew all the answers, at least for our own plant. However, a new 2500-barrels, two-coil Dubbs cracking plant was constructed in August, 1936 which would operate at higher temperatures, velocities, and pressures than the obsolete 500-barrel units that were dismantled. An entirely new set of conditions was presented for protection. This new unit operated four months without any evidence of corrosion above the limits of reasonable tolerance. December 9, 1936, a run was started on this unit. The furnace tubes were all in good condition and apparently the ammonia present as amino compounds in the topped crude was taking care of the corrosive elements present. You will recall that the amino compounds are formed in the crude still by injection of ammonia gas into the crude oil as it enters the furnace.

Exactly 16 days after this run was started the still began leaking badly at the return bends in the furnace. The equipment was shut down and an inspection made. While the still tubes were being unheaded we were surprised to have one of them drop off when the wrenches were applied. Tubes that were originally 5/16-inch thick were found to be about the thickness of sheet tin. Briefly, within a period of 16 days and without any visible warning the entire top bank of still was disintegrated. Thirty-two tubes were removed for replacement.

This cracking still divides the charging stock into a light and a heavy oil which is run through separate furnaces. The corrosion took place in the heavy-oil furnace and in the convection bank. The oil temperature in this region increases from 725° F. to 825° F. The region ranging from 825° F. to 925° F. was not corroded. The pressure within the heavy-oil furnace is usually between 460 and 480 pounds per square inch. Two types of alloy metal are encountered in the furnace. The colder regions are carbon steel and the hotter section carbon molybdenum. The colder section and hotter section both are designed to employ 2⅜-inch I.D. tubes with 5/16-inch wall, while the regions of intermediate temperature use 2⅛-inch I.D. and ¼-inch wall.

In this particular design of furnace we have a unique comparison between the relative value of carbon steel and carbon molybdenum steel. With equal pipe size and despite a temperature handicap of 200° F. the carbon molybdenum steel withstood the corrosive condition in which the carbon steel failed. The factor of turbulence within the tubes was equal —a point which will be discussed shortly. However, we do find that in the smaller-diameter carbon molybdenum tubing we have had some failure, but not quite so severely as with the plain carbon steel which was ¼-inch larger in diameter.

In terms of velocity flow we had severe corrosion in carbon steel with a velocity flow of 6.8 feet per second and practically no corrosion with the same velocity when carbon molybdenum steel is used. However, when the velocity of flow is increased to 7.73 feet per second in the carbon molybdenum alloy tubing it is destroyed approximately as quickly as the carbon steel with a flow velocity of 6.8 feet per second. This comparison shows a decided advantage in favor of the use of carbon molydenum tubes.

While the extremely active corrosion was taking place in the heavy-oil furnace, no deterioration was found in the tubes of the light-oil furnace which operated at almost two times higher pressure, approximately 705 pounds per square inch against 470 pounds per square inch. The inlet and outlet temperatures were approximately identical with the heavy oil furnace.

Judging from a chemical analysis of the end products of the corrosion we were experiencing sulfur corrosion. In our case the principal controlling factor determining the point of attack was the velocity of flow. The furnace construction is such that we have a straight 30-foot flow and then a return bend. Due to the reverse of flow, turbulence of a high order was set up which physically washed away the normal sulfide films that protect the metal from sulfur corrosion. The most severe corrosion extended approximately two feet in the flow direction from the tube return bends.

We are confident that corrosion in the case described was due to direct chemical action of sulfur. In closing the plant down, steam is cut through the still tubes before removal of the headers. This destroyed practically all of the chemical evidence which might have been valuable in assigning the blame for the unusually rapid deterioration. About all that could be learned from our chemical inspection was that iron sulfide was present and the thin coke film over the corroded tubes gave reactions indicating hydrochloric acid. Owing to the steam flushing prior to opening the still, salts, if present at all, were washed away.

An explanation for the complete disintegration of the convection bank in our heavy-oil furnace in the short period of 16 days has never been satisfactorily explained. The corrosion was due to sulfur but the unknown accelerator of this reaction has not been discovered. We do know that free hydrochloric acid was not present, that the salt content of the charge calculated as sodium chloride was 11 pounds per 1000 barrels. The percentage of sulfur present in the topped crude was in the usual normal range of one-half percent. During this critical 16-day period of operation the salt content of our crude oil was checked two times each day. This gave us a means of estimating the daily salt content of the topped crude being run by the cracking unit. There is very little chance of a high magnesium chloride bearing topped crude slipping by our daily salt analysis which might account for the corrosion.

In our opinion none of the known factors accounting for corrosion fit our particular condition. We have formed a rather vague idea of the cause of the trouble being an accelerated sulfur corrosion due to traces of acid salt or perhaps a cyclic sulfur corrosion due to unknown factors. Although an explanation of the cause of our corrosion was an intensely interesting problem the most important factor was to prevent the recurrence of the corrosion. Several refiners in the vicinity of Wichita very generously shared their experiences and information in an effort to assist us in our problem. The consensus of opinion was that approximately ¼-pound of anhydrous lime per barrel of throughput would control our corrosion.

Lime slurry tanks were set up with rotating paddles to maintain an even suspension. Proportioning pumps were installed to feed lime into the heavy-oil and light-oil furnaces. Nearly all commercial chemical lime from the point of view of purity is satisfactory. However, we are attempting to control a

corrosive condition by the addition of an anhydrous chemical whose efficiency is in direct proportion to the amount of surface exposed for chemical action. Limes differ radically in particle size, i.e., available reactive surface per pound. Manufacturers of lime working from the same geological deposit do not necessarily produce lime of equal particle size. We have found it convenient to select our lime by comparing the settling time of the various brands. This was done by suspending equal weights of lime in sample bottles containing a heavy distillate. This method is an easy visual way of judging particle size. Our experience has been that among the dozen or more limes tested two brands are distinctly superior.

A common question among the refineries using lime in their high pressure stills is—when do we have sufficient dosage? Of course the answer is when the corrosive condition is stopped. Only actual experience can prove the presence of sufficient lime dosage. However, we have a system of dosage control which has proved of considerable value.

For each individual high-pressure still the hydrogen sulfide content of the still gases will vary relatively in the proportion as the corrosive sulfur content. Working on the basis of this assumption we measure the hydrogen sulfide content of the still gases and control our lime dosage to hold the sulfide gas to an arbitrary standard. After 10 months of operation without corrosion in our cracking still we believe a hydrogen sulfide content in the still gases of 0.2 pounds per 1000 cubic feet is our permissible tolerance.

In order to develop an arbitrary standard where experience has not proved its worth we suggest that the sulfide content of the still gases be measured during different lime dosages and a curve plotted. Our experience has been that the curve reaches a high point and then flattens out. We assume that beyond this point the lime is of no further benefit. Our present lime dosage to maintain our tolerance of 0.2 pounds hydrogen sulfide per 1000 cubic feet of still gas is 0.32 pounds of anhydrous lime per barrel.

We have found that the lime dosage controlled to a definite hydrogen sulfide tolerance has given excellent protection. The same charging stock which nearly destroyed the heavy oil furnace in a 16-day period has been run through the equipment for 10 months with a tube-wall loss in the order of 2/64-inch. This protection has been given to the following alloy furnace tubes, carbon steel, carbon molybdenum steel, 2 percent chrome and ½ percent molybdenum, Timken Silmo, and D. M. tubes. This assortment of furnace tubes was put into service in January, 1937, at a time when it was impossible to secure full delivery on the types of tubes desired.

SUMMARY

1. We have found the use of ammonia gas of great assistance in the control of sulfur and acid corrosion in crude stills and in low-velocity cracking stills.

2. Corrosive salts in crude oil may be removed conveniently by water scrubbing followed by electrical dehydration.

3. A controlled lime dosage has given excellent protection from corrosion in high-pressure cracking equipment.

As a matter of record the analytical procedures used in our laboratory will be described in brief. We make no claim as to the suitability of these tests for other than practical control work.

BARNSDALL METHOD

Reagents—Silver Nitrate 1 cc equals 1 Milligram Salt.
Potassium Chromate 10% (Indicator)
Bromthymol blue— Hellige
N/50 Sodium hydroxide
C. P. Benzol.

Procedure: 200 cc. Oil to be tested
200 cc. Boiling Dist. Water
100 cc. C. P. Benzol
Shake in a one liter separatory funnel for ten minutes. Mixing with an electric lab. mixer is preferable.

Place the oil emulsion in separatory tubes and shake out on the centrifuge. A small separatory funnel is convenient for dividing the oil from the distilled water which has been thrown down. Occasionally extra heat may be necessary to assist the centrifuge in breaking the emulsion. Titrate 50 cc of the separated water with $AgNO_3$ (1 cc equals 1 milgram salt) using potassium chromate as indicator (1 cc) No. of ccs $AgNO_3$ less blank times 7 equals pounds NaCl per 1000 barrels. **Caution:** Cool the water to room temperature before titrating. For HCl content titrate to exact neutral with bromthymol blue indicator. A Hellige simplex comparator outfit is very convenient for locating exact neutrality. Use Bromthymol blue scale and titrate to exactly 7 pH. A 1 cc pipette graduated to 1/100 cc is used for measuring the quantity of N/50 caustic necessary. No. cc N/50 NaOH times 5.11 equals pounds HCl per 1000 barrels. Hydrogen ion concentration is measured on the extract water and recorded as pH of crude. Hot boiling water must be used for the crude extraction to prevent solution of hydrogen sulfide.

When everything is set up a complete analysis may be made in one hour. If it is desirable to separate the salts into their respective compounds, double the volumes in the original extraction.

Two hundred ml. of the extract is placed in a 400 ml. beaker to which is added 10 ml. of 30 percent acetic acid and 1 gram of ammonium chloride. Bring to a boil, add 15 ml. of saturated oxalic acid solution, let stand for 5 minutes and add a slight excess of ammonium. After 4 hours filter into a weighed Gooch crucible and blast for 1 hour, cool in a desiccator and weigh as calcium oxide. Convert this weight to calcium chloride and calculate to pounds per 1000 barrels.

The filtrate from the calcium determination is made slightly acid, add an excess of 10 percent disodium phosphate solution, stir constantly while adding, allow the solution to stand for 5 minutes and then add concentrated ammonium hydroxide in the proportion of one volume to two volumes of the filtrate. After standing 3 hours or more the precipitate is filtered out on a weighed Gooch crucible, blasted for 1 hour, cooled in the desiccator and weighed as $Mg^2 P_2 O_2$ which is then converted to magnesium chloride and calculated as pounds per 1000 barrels of crude oil.

Determination of hydrogen sulfide in still gas may be made rapidly in the Tutweiler gas analysis apparatus which works on the principle of the oxidation of hydrogen sulfide gas by astandardize iodine solution. This anlysis may be made in approximately 5 minutes. Although the accuracy is not suitable for exact work it will suffice for plant control of a hydrogen sulfide tolerance in still gases. We prefer to calculate the results as pounds per 1000 cubic feet of gas.